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ORGANIC BY-PRODUCT FORMATION FROM THE OZONATION AND CHLORINATION OF AQUATIC NATURAL ORGANIC MATTER

BY

SUSAN ALEXANDRA ANDREWS ©

A thesis submitted to the Faculty of Graduate Studies and research in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

IN

ENVIRONMENTAL SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

EDMONTON, ALBERTA

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DEDICATION

This dissertation is dedicated to the memory of

Shirley Anne Daignault

who wanted us to believe in ourselves
and who always supported us, whatever our dreams.

ABSTRACT

An improved procedure was developed and applied to fractionate natural organic matter (NOM) prior to characterization and subsequent ozonation under conditions representing typical drinking water treatment practice. Two surface waters, each a source of potable water, were investigated. One was a eutrophic lakewater with characteristic late summer non-volatile dissolved organic carbon (NVDOC) concentrations of 10 to 15 mg C/L. The other was a river water with a much lower NVDOC (2 to 5 mg C/L during most seasons).

NOM was fractionated using Amberlite® XAD-8 resin followed by XAD-4 and cation exchange (Bio Rad® AG MP-50). At pH 2, the XAD resins isolate acidic and hydrophobic NOM (humic and fulvic acids), whereas the cation exchange concentrates hydrophilic bases. Improving the procedure by incorporating XAD-4 and AG MP-50 resins allowed a significantly higher amount of NOM to be recovered and fractionated. Using this additional material a more thorough investigation of disinfection by-product (DBP) precursors could be attempted. When compared to previously reported fractionation procedures utilizing XAD-8 resin, the yield of XAD-isolable material approximately doubled with the addition of XAD-4 resin, and increased a further 25 % when ion exchange was included.

NOM isolated on XAD-4 resin was similar in character to that isolated on XAD-8, but displayed a lower molecular weight and higher aliphatic content (as determined by infrared spectroscopy) than that isolated on XAD-8. The characteristics of the hydrophilic bases isolated on AG MP-50 resin were different from those of the XAD-isolates, most notably in their greater aliphatic content when compared to the XAD-4 fractions, and in their substantially higher nitrogen content.

Bench scale ozonation experiments were conducted under various conditions of pH, alkalinity (total carbonate species concentration) and ozone dosage to assess by-product formation for a range of possible process conditions. Classes of DBPs which were measured included aldehydes, oxoacids and low molecular weight carboxylic acids. Several samples were also post-chlorinated or post-choraminated to simulate typical drinking water treatment conditions. These were examined for the production of DBPs including trihalomethanes, haloacetic acids, chloral hydrate and cyanogen chloride.

Of the ozonation parameters studied, pH was shown to exert the largest effect on both ozonation and post-chlor(am)ination DBP formation. Greater amounts of ozonation DBP precursors were generally isolated using the XAD-4 resin when compared to the XAD-8. This was true for both water sources and for all DBP classes. Lakewater NOM generally produced more DBPs per mass than did river water NOM. In contrast, higher amounts of precursor material for the halogenated DBPs, especially following ozonation, were isolated on the XAD-8 resin and from river water. These results illustrate the dependence of DBP formation on source water characteristics as well as the precursor isolation method employed. DBP yields were not directly related to the concentrations of precursor material utilized, emphasizing some of the problems of extrapolating data obtained at bench scale to conditions encountered in typical water treatment.

In summary, NOM was isolated from a eutrophic lakewater and from river water, both sources of potable water. To improve the recovery of NOM, Amberlite® XAD-4 and Bio Rad® AG MP-50 resins, in addition to XAD-8 were used for NOM fractionation. Solutions of fractionated material were ozonated, and in some cases subsequently chlorinated or chloraminated to investigate the origins of various classes of DBPs of interest in drinking water treatment.

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I would also like to thank the other members of my advisory committee for providing insight into many areas of my research. In particular, acknowledgement and appreciation is extended to Dr. D.T. Williams, Health and Welfare Canada, for providing guidance and financial support for the research contract which formed the basis of this dissertation.

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Finally, I would like to thank Dr. R.C. Andrews, whose pursuit of excellence is truly inspirational, and whose motivation to achieve is contagious. His many and varied interests continue to add new dimensions to my life, and his support of my efforts in this research has been unfailing.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

1 LITERATURE REVIEW 1

1.1 Overview 1

  1.1.1 Ozone in Drinking Water Treatment: The By-Products Issue 1

  1.1.2 General Ozone Reaction Mechanisms 7

1.2 Organic By-Products of Ozonation 10

  1.2.1 Hydrocarbons 12

    1.2.1.1 Alkanes, Alkenes, and Alkynes 12

    1.2.1.2 Aromatic Compounds 12

  1.2.2 Oxygen-Containing Molecules 13

    1.2.2.1 Aldehydes, Acids, Ketones, Furans, Alcohols and Ethers 13

    1.2.2.2 Phenols 16

  1.2.3 Nitrogen-Containing Molecules 17

    1.2.3.1 Amino Compounds 18

    1.2.3.2 Nitro Compounds 18

    1.2.3.3 Carbamates, Amino Acids 20

    1.2.3.4 Heterocycles 20

1.3 Reactions of Ozone with Humic and Fulvic Materials 22

  1.3.1 Humic Content Overview 22

  1.3.2 Known Reaction By-Products 28

1.4 Algogenic Material 31

  1.4.1 Overview 31

  1.4.2 Effects of Ozonation 33

1.5 Chlorination and Chloramination By-Products of Humic/Fulvic Acids 34

1.6 Analytical Methods for Known and Expected By-Products.......... 37
1.7 Summary and Identification of Research Needs.......... 40
2 RESEARCH OBJECTIVES.......... 44
3 MATERIALS AND METHODS.......... 46
3.1 Reagents and Glassware.......... 46
3.2 Isolation and Characterization of Aquatic Natural Organic Matter.......... 47
    3.2.1 Sampling.......... 47
    3.2.2 Filtration.......... 48
    3.2.3 XAD Resin Adsorption (Humic and Fulvic Acid Isolation).......... 50
    3.2.4 XAD Resin Elution.......... 53
    3.2.5 Separation of Humic and Fulvic Acids.......... 54
    3.2.6 Desalting, Hydrogen-Saturation and Freeze-Drying.......... 55
    3.2.7 Resin Cleaning and Isolation of Hydrophobic Neutral Components.......... 56
    3.2.8 Cation Exchange Resin Isolation of Hydrophilic Bases.......... 57
    3.2.9 NOM Fraction Characterization Methods.......... 61
3.3 Ozonation Procedures.......... 63
    3.3.1 Factorial Design.......... 64
    3.3.2 Ozonation of 20 mg/L NVDOC Fulvic Acid Solutions.......... 66
    3.3.3 Ozonation of 5 mg/L NVDOC Fulvic Acid Solutions.......... 68
    3.3.4 Post-Ozone Chlorination and Chloramination.......... 70
3.4 Disinfection By-Products Analyses.......... 70
    3.4.1 Ozonation By-Products.......... 70
        3.4.1.1 Aldehydes.......... 72
        3.4.1.2 Oxoacids.......... 73
        3.4.1.3 Carboxylic Acids.......... 73
    3.4.2 Chlorination and Chloramination By-Products.......... 80
        3.4.2.1 Cyanogen Chloride.......... 82

3.4.2.2 Trihalomethanes 82

3.4.2.3 Haloacetic Acids 84

3.4.2.4 Chloral Hydrate 84

3.4.2.5 Chloro-oxoacids and Chlorophenols 84

3.5 QA/QC 85

3.5.1 Reagents 85

3.5.2 NOM Isolation 86

3.5.3 NOM Characterization 87

3.5.4 Ozonation Experiments 87

3.5.5 DBPs Analyses 88

4 ISOLATION, FRACTIONATION AND CHARACTERIZATION OF NOM FROM RIVER WATER AND LAKEWATER 90

4.1 Resin Capacity Calculations and Tests 90

4.2 NOM Isolation 97

4.2.1 Raw Water Quality Data 98

4.2.2 Adsorption Monitoring Data 98

4.2.3 Fraction Yields 102

4.2.4 Characterization of Fractions 104

4.2 Summary 110

5 ORGANIC DBPS RESULTING FROM THE OZONATION OF ISOLATED NOM FRACTIONS AND NATURAL WATER MATRICES 112

5.1 Ozonation of Isolated Fulvic Acids at 20 mg/L NVDOC 114

5.1.1 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance 115

5.1.2 Aldehyde, Oxoacid and Carboxylic Acid Production 120

5.1.3 Correlations Between UV Absorbance and DBP Formation 126

5.1.4 Ozonation Parameter Interactions 126

5.2 Ozonation of Isolated Fulvic Acids at 5 mg/L NVDOC 130

5.2.1 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance 131

5.2.2 Aldehyde, Oxoacid and Carboxylic Acid Production 134

5.2.3 Correlations Between UV Absorbance and DBP Production 140

5.3 Ozonation of Natural Waters 141

5.3.1 Natural Water Characteristics 141

5.3.2 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance 143

5.3.3 Aldehyde, Oxoacid and Carboxylic Acid Production 147

5.4 Summary 152

6 EFFECT OF NOM CONCENTRATION ON ORGANIC OZONATION BY-PRODUCT FORMATION AND UV ABSORBANCE REDUCTION 155

6.1 NOM Concentration and UV Absorbance Reduction 156

6.2 Organic By-Product Results 158

6.2.1 Results of All Classes of DBPs 158

6.2.2 Ketomalonic Acid Formation 162

6.3 Summary 164

7 EFFECTS OF OZONATION ON THE FORMATION OF HALOGENATED DBPS FROM CHLORINATION OR CHLORAMINATION 166

7.1 Post-Ozone Chlorination 167

7.1.1 Effects of Ozonation Parameters on Oxidant Demand 169

7.1.2 Effects of Ozonation Parameters on XDBP Formation Potential 171

7.2 Post-Ozone Chloramination 185

7.2.1 Effects of Ozonation Parameters on Oxidant Demand 185

7.2.2 Effects of Ozonation Parameters on XDBP Formation Potentials 186

7.3 Summary 194

8 CONCLUSIONS 197

8.1 Precursor Concentration Effects 197

8.2 Effects of Ozonation Parameters on Colour and DBPs 197

8.3 Effect of Ozonation on Chlorine Demand and XDBP Production 199

8.4 Effectiveness of NOM Isolation Procedures 201

9 RECOMMENDATIONS 203

9.1 Experimental Conditions 203

9.2 Full Scale Drinking Water Treatment 203

9.3 Future Research 205

REFERENCES 207

APPENDIX I Additional QA/QC and Analytical Methods Development Information 224

APPENDIX II NOM Adsorption Monitoring Data 251

APPENDIX III NOM Fraction Characterization Data 266

APPENDIX IV UV Absorbance and Disinfection By-Products from the Ozonation of NOM Fractions and Water From Driedmeat Lake and the North Saskatchewan River 284

APPENDIX V Effect of NVDOC Concentration on Organic Ozonation By-Product Formation (Data at pH 8) 302

APPENDIX VI Halogenated Disinfection By-Products from Ozonation and Chlorination of Isolated NOM and of Water From Driedmeat Lake and the North Saskatchewan River 305

APPENDIX VII Halogenated Disinfection By-Products from Ozonation and Chloramination of Isolated NOM and of Water From Driedmeat Lake and the North Saskatchewan River 320

LIST OF TABLES

Table Page

1.1 Analytical Methods for the Determination of Carboxylic Acids in Water 37

3.1 Relative Affinities of Bio Rad AG MP-50 Resin for Cations 59

3.2 Parameters and their Values Employed in the Factorial Design Experiments 65

3.3 Ozonation By-Products 71

3.4 Halogenated Disinfection By-Products 81

4.1 Water Quality Data for Driedmeat Lake and the North Saskatchewan River 99

4.2 Mass of Freeze-Dried NOM Fractions Isolated from Driedmeat Lake and the North Saskatchewan River 103

4.3 Elemental Analysis and Average Molecular Weight of Fulvic Acids and Hydrophilic Bases 106

4.4 UV Absorbance Data 108

5.1 Organic Ozonation Compounds 113

5.2 Characteristics of Waters Obtained from the North Saskatchewan River and Driedmeat Lake 144

7.1 Halogenated Disinfection By-Products 168

LIST OF FIGURES

Figure Page

1.1 Ozone's Participation in Free Radical Reactions.................................... 9

1.2 Distribution of Surface Water Dissolved Organic Carbon in Rivers of the United States.. 23

1.3 Proposed Structure of Colour Macromolecule.. 24

1.4 Suggested Chemical Structure of Fulvic Acid 24

1.5 Proposed Tetramer Structure for Humic Acid 25

1.6 Change in Molecular Weight Distribution on Ozonation........................... 32

3.1 Apparatus Used to Filter Raw Water Samples Prior to NOM Isolation........... 49

3.2 Apparatus for Isolation and Fractionation of Natural Organic Matter.............. 51

3.3 Effluent Concentrations of Sodium Ion Measured During Upflow and Downflow Ion Exchange Experiments 62

3.4 Change in Post-Ozonation UV Absorbances of Four Samples of Lakewater with Time... 69

3.5 Schematic Illustrating Methodology for Determining Oxoacids 74

3.6 Schematic Illustrating Methodology for Determining Carboxylic Acids........... 75

3.7 Effect of Tetrabutylammonium Hydrogen Sulfate Concentration on the Formation of Pentafluorophenol Ester of Acetic Acid 77

3.8 Effect of Salt Concentration on the Formation of Pentafluorophenol Ester of Acetic Acid in the Presence of 0.5 mg/mL TBAHS.................................. 77

3.9 Kinetics of Formation of Pentafluorophenol Ester of Acetic Acid.................. 79

3.10 Effect of Ionic Strength on Cyanogen Chloride Extraction Efficiency............. 83

4.1 Preliminary Breakthrough Curve for Adsorption of NOM from Driedmeat Lake Water on XAD-8 Resin 94

4.2 Preliminary Breakthrough Curve for Adsorption of NOM from North Saskatchewan River Water on XAD-8 Resin... 94

4.3 Idealized Breakthrough Curve for Stream Humic Substances on XAD-8 Resin.. 95

4.4 Extent of Breakthrough for 400 mL Test Water on 10 mL XAD-8 Resin Columns... 96

4.5 Non-Volatile Dissolved Organic Carbon Monitoring Data for Filtered Lakewater 101

4.6 UV Absorbance Adsorption Monitoring Data for Filtered Lakewater........ 101

5.1 Effect of pH, Alkalinity and Ozone Dose on Reduction of UV Absorbance of NOM Fractions at 20 mg/L NVDOC. 116

5.2 Effects of pH, Alkalinity and Ozone Dose on Formation of Aldehydes During Ozonation of NOM Fractions at 20 mg/L NVDOC........ 121

5.4 Effects of pH, Alkalinity and Ozone Dose on Formation of Carboxylic Acids During Ozonation of NOM fractions at 20 mg/L........ 122

5.5 Main Effects of Increasing pH from 6 to 8 on DBP Formation for Four Different Fulvic Acids at 20 mg/L NVDOC........ 122

5.6 Response Surface for Interaction of Alkalinity and pH on Aldehydes Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin........ 127

5.7 Response Surface for Interaction of Alkalinity and pH on Aldehydes Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin........ 127

5.8 Response Surface for Interaction of Alkalinity and pH on Oxoacids Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin........ 128

5.9 Response Surface for Interaction of Alkalinity and pH on Oxoacids Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin........ 128

5.10 Effect of pH, Alkalinity and Ozone Dose on the Reduction of UV Absorbance (254 nm) on NOM Fractions at 5 mg/L NVDOC 132

5.11 Effect of pH on the Formation of DBPs from the Ozonation of NOM Fractions at 5 mg/L NVDOC........ 135

5.12 Effect of Alkalinity on the Formation of DBPs from Ozonation of NOM Fractions at 5 mg/L NVDOC........ 135

5.13 Effect of Ozone Dose on the Formation of DBPs from Ozonation of NOM Fractions at 5 mg/L NVDOC........ 136

5.14 Effect of Various Parameters on the Formation of Aldehydes from the Ozonation of NOM Fractions 136

5.15 Effect of Various Parameters on the Formation of Oxoacids from the Ozonation of NOM Fractions 137

5.16 Effect of Various Parameters on the Formation of Carboxylic Acids from NOM Fraction Ozonation........ 137

5.17 Correlations Between UV Reduction and Oxoacids Production on Ozonation of Various Fractions of NOM at 5 mg/L NVDOC........................ 142

5.18 Effect of pH, Alkalinity and Ozone Dose on Reduction of UV Absorbance of Natural Source Waters... 145

5.19 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Aldehydes During Ozonation of Natural Waters..................................... 148

5.20 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Oxoacids During Ozonation of Natural Waters 148

5.21 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Carboxylic Acids During Ozonation of Natural Waters............................. 149

6.1 Reduction in Lakewater Fulvic Acid UV Absorbance as a Function of NVDOC Concentration and pH.. 157

6.2 Effect of NVDOC Concentration on Formaldehyde and Acetaldehyde Formation 159

6.3 Effect of NVDOC Concentration on Glyoxal and Methyl Glyoxal Formation 159

6.4 Effect of NVDOC Concentration on Oxoacid Formation............................. 160

6.5 Effect of NVDOC Concentration on Carboxylic Acid Formation 160

6.6 Aqueous Redox of Quinone-Type Moieties of Fulvic Acids Showing Semiquinone Intermediates... 163

6.7 Proposed Reaction Scheme for the Formation of Ketomalonic Acid from Fulvic Acid.. 163

7.1 Effect of pH on the Chlorine Demand of Ozonated NOM Fractions 170

7.2 Changes in Chlorine Demand on Ozonation of NOM Fractions..................... 172

7.3 Effect of pH on the Formation of Trihalomethanes from the Ozonation of NOM Fractions 174

7.4 Effect of Alkalinity on the Formation of Trihalomethanes from the Ozonation of NOM Fractions 174

7.5 Effect of Applied Ozone Dose on the Formation of Trihalomethanes from the Ozonation of NOM Fractions.. 175

7.6 Effect of pH on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions 178

7.7 Effect of Alkalinity on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions 178

7.8 Effect of Ozone Dose on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions 179

7.9 Effect of pH on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions 181

7.10 Effect of Alkalinity on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions 184

7.11 Effect of Ozone Dose on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions 184

7.12 Effect of pH and Type of Oxidant used on THMFP 187

7.13 Effect of Alkalinity and Type of Oxidant used on THMFP 187

7.14 Effect of Ozone Dose and Type of Oxidant used on THMFP 188

7.15 Effect of pH and Alkalinity on THMFP of Non-Ozonated NOM Fractions 188

7.16 Effect of pH and Type of Oxidant used on HAAFP 190

7.17 Effect of Ozone Dose and Type of Oxidant used on CHFP 190

7.18 Effect of pH on the Formation of Cyanogen Chloride from the Ozonation of NOM Fractions 191

7.19 Effect of Alkalinity on the Formation of Cyanogen Chloride Following the Ozonation of NOM Fractions 191

7.20 Effect of Applied Ozone Dosage on the Formation of Cyanogen Chloride Following the Ozonation of NOM Fractions 192

7.21 Effect of pH and Ozone on the Formation of Cyanogen Chloride in Natural Water Matrices 195

LIST OF SYMBOLS

AG MP-50 = Bio Rad® AG MP-50 cation exchange resin

AOC = assimilable organic carbon

AWWA = American Water Works Association

BrAA = bromoacetic acid

C/C_0 = concentration (C) relative to the influent concentration (C_0)

CI = confidence interval

DBP = disinfection py-product

DBPFP = disinfection by-product formation potential

DCAA = dichloroacetic acid

DCC = dicyclohexylcarbodiimide

DML = Driedmeat Lake

DML4,L-4 = sample associated with Amberlite® XAD-4 extract of Driedmeat Lake water

DML8,L-8 = sample associated with Amberlite® XAD-8 extract of Driedmeat Lake water

DNA = deoxyribonucleic acid

DOC = dissolved organic carbon

EOM = extracellular organic matter

EPA = Environmental Protection Agency

FT-IR = Fourier-transform infrared spectrum or spectroscopy

GC/ECD = gas chromatography with electron capture detection

GC/FID = gas chromatography with flame ionization detection

H^+ = hydrogen ion

$[H^+]$ = hydrogen ion concentration

HAA = haloacetic acid

HAAFP = haloacetic acid formation potential

$HO\cdot$ = hydroxyl radical

$HOO\cdot$ = hydroperoxyl radical

HPLC = high performance liquid chromatography

I.S. = internal standard

IHSS = International Humic Substances Society

k' = adsorption column capacity factor

K^+ = potassium ion

L-4, DML4 = sample associated with Amberlite® XAD-4 extract of Driedmeat Lake water

L-8, DML8 = sample associated with Amberlite® XAD-8 extract of Driedmeat Lake water

MBA = mucobromic acid

MCL = maximum contaminant level

mmho, μmho = unit of conductivity, 10^{-3} or 10^{-6} x 1/resistivity

MNNG = 1-methyl-3-nitro-1-nitrosoguanidine

MTBE = methyl-*t*-butyl ether

MW = molecular weight

MX = mutagen 'X', 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)furanone

Na^+ = sodium ion

NA, N/A = not available or not applicable

n_i = number of observations of type i

NMR = nuclear magnetic resonance

NOM = natural organic matter

NSR = North Saskatchewan River

NSR4,R-4 = sample associated with Amberlite® XAD-4 extract of North Saskatchewan River water

NSR8,R-8 = sample associated with Amberlite® XAD-8 extract of North Saskatchewan River water

NSRX = sample associated with ion exchange extract of North Saskatchewan River water

NVDOC = non-volatile dissolved organic carbon

O_3 = ozone

ODF = ozone demand free

OH^- = hydroxide ion

PFBOA = O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride

PFP = pentafluorophenol

QA/QC = quality assurance and quality control

R-4, NSR4 = sample associated with Amberlite® XAD-4 extract of North Saskatchewan River water

R-8, NSR8 = sample associated with Amberlite® XAD-8 extract of North Saskatchewan River water

r^2 = correlation coefficient

RCI = confidence interval relative to the factorial mean

RSD = relative standard deviation

SFC = supercritical fluid chromatography

s_i = standard deviation of observations of type i

TBAHS = tetrabutylammonium hydrogen sulfate

TCAA = trichloroacetic acid

$t_{df,\alpha/2}$ = student 't' statistic, obtained at an appropriate number of degrees of freedom (df) and level of significance ($\alpha/2$)

THM = trihalomethane

THMFP = trihalomethane formation potential

TOC = total organic carbon

TOX = total organic halide

UV = ultraviolet

UV/VIS = ultraviolet and visible

Var $\bar{y}$ = variance in the values determined for the midpoints of the factorial experiments

V_e = maximum sample volume sorbable to ion exchange resin prior to 50% breakthrough

V_E = maximum sample volume sorbable to Amberlite XAD resins prior to 50% breakthrough

V_o = resin column void volume

XAD-8 = Amberlite® XAD-8 resin

XAD-4 = Amberlite® XAD-4 resin

XDBP = halogenated disinfection by-product

XDBPFP = halogenated disinfection by-product formation potential

CHAPTER 1

LITERATURE REVIEW

1.1 Overview

This review deals primarily with reaction mechanisms and organic by-products of the aqueous ozonation of natural organic matter (NOM). The oxidation of organic compounds is not a new field of study and this review is not meant to be a repetition of long established oxidative reactions. Instead, attempts have been made to present examples appearing in the literature which discuss reaction mechanisms and by-products of NOM ozonation, including some discussion of ozone's reaction with relatively small molecules expected to be constituents of NOM. Inorganic ozonation chemistry and health effects are discussed only where direct relevance to the proposed research has been demonstrated.

1.1.1 Ozone in Drinking Water Treatment: The By-Products Issue

1.1.1.1 Ozone Alone

The discovery of trihalomethanes (THMs) in drinking water and investigation of carcinogenic risk associated with their ingestion fueled the pursuit of means to reduce or eliminate both THMs and other recently identified chlorination disinfection by-products (DBPs) of health concern. In looking to alternative disinfectants as one possible solution to this problem, ozone has shown much promise in reducing the formation of these DBPs (Cook, 1989; Rice, 1991). It has been used successfully as a drinking water disinfectant in many European countries since the early 1900s, although research into DBPs related to ozonation practise has only recently been initiated. The delay occurred because ozone does not normally produce halogenated by-products, and because it was considered a more "natural" oxidant which produced many biodegradable by-products. In addition, it has only been recent advancements in analytical chemistry that have made such research more feasible.

Ozonation of natural organic matter (NOM) can lead to the production of by-products which are either toxicologically or otherwise biologically significant. During drinking water disinfection, NOM reacts with ozone in both molecular form and as hydroxyl radicals to form oxygenated DBPs having reduced colour and molecular weight (Anderson *et al.*, 1986a; Bedessem *et al.*, 1989). Aldehydes, ketones and carboxylic acids are all formed during ozonation of aquatic NOM (Glaze, 1986; Matsuda *et al.*, 1992; Coleman *et al.*, 1992). Toxicological data on these by-products are limited, but they show that some DBPs could be of health concern. Aldehydes, including for example formaldehyde, acetaldehyde, glyoxal and methylglyoxal, are known or suspected mutagens and carcinogens (Bull and Kopfler, 1991; Cajelli *et al.*, 1987; Sayato *et al.*, 1987). Carboxylic acids are not considered a direct toxicological hazard (Bull and Kopfler, 1991) but may be a significant component of the substrate (termed assimilable or easily biodegradable organic carbon) for growth of microbes in the distribution system which can deteriorate the quality of the distributed water.

Although there are many factors influencing the microbial stability of finished drinking water, the limiting factor is often the amount of biodegradable organic matter available. A variety of tests have been developed to estimate the amount of this material in water and/or to measure biomass produced (Huck, 1990, Anderson *et al.*, 1990a). All of these tests are a measure of overall biodegradability, and are not able to identify individual classes of organic compounds.

The use of ozone in drinking water treatment has been shown to be effective in many applications, including taste and odour control, colour, iron and manganese removal, THM precursor control and as a coagulant aid. It effectively removes many classes of compounds from water. For example Lykins and Koffskey (1985) reported on the performance of a pilot plant employing several alternative disinfectants, including ozone. They found that ozone reduced the concentrations of several classes of both natural and synthetic organic chemicals. Compounds included in the study were chlorinated pesticides such as atrazine (83% reduction on ozonation) and alachlor (84%), alkyl benzenes (52%), alkanes (35%), phthalates (11%), chlorobenzenes (68%) and nitrobenzenes (61%). The only class of compounds studied which showed an increase in concentration upon ozonation was the alkylaldehydes (144%). Specific degradation by-products were generally not identified in this work.

In addition to its properties as a disinfectant, ozone applied early in a treatment sequence has been shown to enhance coagulation and flocculation (Edwards and Benjamin, 1991; Jekel, 1991; Grasso and Weber, 1988; Richard, 1992; Reckhow *et al.*, 1986; Glaze, 1987; Chen *et al.*, 1987). This use of ozone is termed pre-ozonation, because ozone application in such instances is usually applied prior to the primary disinfectant which may or may not be ozone. Several of these researchers have postulated that ozone oxidizes humic material to form polar chelating groups which are effective in aiding coagulation. However, pre-ozonation has its drawbacks. For example, Janssens *et al.* (1987) reported the formation of low molecular weight aldehydes (formaldehyde and acetaldehyde) and short chain carboxylic acids on pre-ozonation, compounds which can contribute to the instability of finished drinking water. While filtration often results in the removal of these by-products, their formation may be cause for concern especially if filtration is unavailable.

Ozone has also been shown to be an effective agent for reducing many taste and odour compounds. For example Anselme *et al.* (1988) showed that musty, earthy, fishy and muddy tastes and odours were all removed by ozone treatment. However, plastic and astringent tastes were not as well removed, and fruity odours were actually enhanced by ozone treatment. Flavour profile analysis and chemical testing showed that fruity and fragrant odours were caused by formation of various aldehydes while plastic odours were associated with phenolic or ethoxy compounds.

There has been some concern over possible adverse health effects of these DBPs for humans. For example, formaldehyde is a commonly detected ozonation by-product which has been reported to be both toxic and carcinogenic, and unsaturated aldehydes such as acrolein have known hepatotoxic properties (National Research Council, 1980). The U.S. Environmental Protection Agency is considering regulating a number of these compounds (Pontius, 1990) even though analytical techniques for all of them do not as yet exist. However, Glaze *et al.* (1989b), in outlining several advantages and disadvantages of ozone disinfection and predisinfection, have also commented on the disinfection by-products observed to date. They state that these by-products, including aldehydes, carboxylic acids and ketones, are generally the same as those encountered during natural oxidation of organic material and as such may have little health significance. These researchers also noted that "our knowledge of ozone by-products is limited by the choice of analytical methods used in prior studies." For example, brominated organic by-products, peroxides and epoxides were also suggested to be of interest but methods of analysis were limited at the time of writing.

The advent of short term bioassays such as the Ames mutagenicity test has enabled the evaluation of possible health effects of various water treatment technologies, including ozonation (Noot *et al.*, 1989). While suffering from the limitation of not being directly applicable to human health, these tests have been used as warning flags for possibly harmful by-products or by-product synergisms, without having to actually isolate and identify all such possible by-products.

These short term bioassays have generally indicated that ozone does not increase mutagenicity; however one should consider the sample preparative procedures which were employed when interpreting data reported in the literature. For example, the relative effects of four different disinfectants on the resulting mutagenicity of drinking water prepared at a pilot plant in Edmonton, Alberta were studied (Huck, 1986; Huck *et al.*, 1988, Anderson *et al.*, 1990b). Chlorine, chlorine dioxide, chloramines and ozone were the disinfectants used in the comparison. Neutral disinfection by-products were targetted for investigation because they had previously been reported by many researchers to be the class of organics containing the greatest number of mutagens, especially in studies of chlorination. Neutral organic disinfection by-products were isolated by adsorption onto Amberlite® XAD-2 resin at ambient pH. The results showed that ozone did not produce any neutral compounds that were mutagenic by the Ames test while other disinfectants did produce neutral fraction mutagenicity.

Similar studies performed by others include that by Kool and Van Kreijl (1984) which showed that ozonation decreased mutagenicity of water compared to untreated water. Again, samples were preconcentrated on Amberlite® XAD-4 and XAD-8 resin for the study isolating mostly non-polar constituents. Also, Backlund *et al.* (1985) found that organics concentrated from ozone-treated water onto Amberlite® XAD-4 and XAD-8 resins did not exhibit mutagenicity, and that pre-ozonation did not alter the mutagenicity detected following post-chlorination (except at high ozone doses which resulted in slightly reduced mutagenicity). The results of these studies generally confirm those of others (Zoeteman *et al.*, 1982; Kool, *et al.*, 1982; Van Hoof, 1983; Van der Gaag *et al.*, 1985) however inconsistencies in the results of several researchers have been noted (Dolara *et al.*, 1981; Van Hoof, 1983; Meier and Bull, 1984; Van der Gaag *et al.*, 1985; Cognet *et al.*, 1986; Janssens *et al.*, 1987). For example, Janssens *et al.* (1987) found that increasing doses produced more by-products (aldehydes, carboxylic acids) and more mutagenicity, suggesting that the by-products detected in this case could be at least partially responsible for the mutagenicity. Causes for the discrepancies in the observed results were speculated to be differing water source characteristics and varying analytical methods employed (for example, sample preconcentration methods).

1.1.1.2 Ozone In Combination with a Chlorine-Based Disinfectant

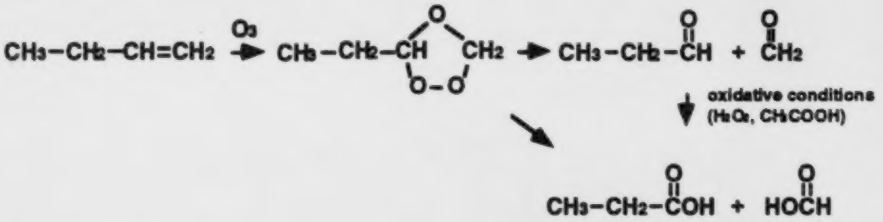
As the half life of ozone is very short, being on the order of minutes at typical drinking water treatment pH (less than 7 minutes as reported by Gilbert *et al.*, 1990), utilities employing ozone for disinfection will be required to use another disinfectant for maintenance of a residual in the distribution system. This will typically be accomplished by application of either chlorine or chloramines.

Studies concerning the effect of ozonation on mutagenicity resulting from subsequent chlorination have provided varying results. Kowbel *et al.* (1982, 1984, 1986) studied the effect of pre-ozonation on the mutagenicity of isolated fulvic acids which were subsequently chlorinated. While specific disinfection by-products were not identified, Kowbel *et al.* (1986) generally found that ozonation of fulvic acid at high pH (pH 8) prevented subsequent formation of chlorination by-products, as indicated by measurements of mutagenicity, and that ozonation on its own produced non-mutagenic or sometimes weakly mutagenic material. Mutagenicity decreased as the pH during ozonation increased (pH 4 to 8 were studied), which they presumed to be due to greater amounts of hydroxyl radical and superoxide radical ion formation at the higher pH. Samples in these studies were rotovapped dry prior to mutagenicity testing which may have affected results. Ozonation was previously reported to either increase (Gruener 1978; Carlberg, 1981) or decrease (Zoeteman, 1982; Denkhaus, 1980) resulting mutagenicity, where many different factors could account for the discrepancies.

In consideration of specific by-products resulting from drinking water treatment, studies have shown that ozonation DBPs can react with chlorine to form halogenated DBPs, including for example chloropicrin and trihalomethanes (Glaze, 1988). However, the quantities of trihalomethanes formed on ozone application followed by post-chlorination and/or post-chloramination have usually been much less than those formed by the application of chlorine or chloramines alone (Huck, 1986; Huck *et al.*, 1988; Amy *et al.*, 1987, 1988). In addition, monochloramine is resistant to reaction with ozone, making the ozone/monochloramine combination good for primary and distribution system disinfection (Haag and Hoigné, 1983; Singer 1988b). However, all of the by-products formed by the ozone/chlorine or ozone/chloramine disinfectant combination may not be the same as in the case of chlorine or chloramine disinfection alone.

1.1.2 General Ozone Reaction Mechanisms

There are two generally accepted mechanisms of ozonation reactions: (1) involving molecular ozone and (2) by free radical reactions (references including Maggiolo, 1978; Glaze, 1986; Hoigné and Bader 1976). The mechanism by which molecular ozone reacts at sites of unsaturation, referred to as the ionic mechanism by Maggiolo (1978), has been referred to by most others as either ozonolysis or the molecular mechanism. It occurs at pH less than 6 (Rice and Gomez-Taylor, 1986) or pH less than 8 (Maggiolo, 1978), and if there are no or few metal ions present (Maggiolo, 1978). The molecular reaction results in the formation of ketones, aldehydes and hydroxyhydroperoxides, the latter two of which can react further in the presence of the excess oxygen usually present during ozonation to form primarily acids and ketones. The following is an example of the molecular reaction scheme.



In the presence of metal ions, oxygen, sunlight, peroxides and at pH greater than 9 (Maggiolo, 1978) or pH greater than 8 (Rice and Gomez-Taylor, 1986), the free radical pathway is favoured. At high pH, ozone reacts with water to form quantitatively equal amounts of hydroxyl (HO·) and hydroperoxide radicals (HOO·). These radicals behave less predictably than the ozone molecule but will generally either add to unsaturated sites or abstract active hydrogens from molecules. Oxygen, a major by-product of ozonation (Rice and Gomez-Taylor, 1986), also participates in the free radical pathway and can act in the formation of organic hydroperoxides, which degrade to aldehydes and ketones. Also, in combination with ultraviolet irradiation or hydrogen peroxide application, ozone produces even more hydroxyl radicals (Rice and Gomez-Taylor, 1986), promoting the free radical reaction pathway.

The molecular (direct) and free radical reaction pathways are illustrated in Figure 1.1. The relative importance of the free radical vs ozonolysis mechanisms for typical drinking water treatment conditions is dependent on various raw water quality parameters. It has also been suggested that even when molecular reactions are initially predominant, organic and inorganic radicals are generated which participate in subsequent oxidations (Staehelin and Hoigné, 1982; Buhler *et al.*, 1984; Staehelin *et al.*, 1984).

Maggiolo (1978) reviewed the two general mechanisms of ozonation, which she termed radical and ionic, and suggested ways to minimize toxic by-products such as epoxides. In her review she emphasizes that by-products identified in the early literature for which organic solvents were generally used (for example ozonides, peroxides and epoxides) are not necessarily going to be observed in samples of ozonated drinking water or wastewater due to the fact that water will participate in the reaction in the latter case to a significant extent. Much of the early research on ozonation reaction mechanisms, pathways and by-products was conducted in non-aqueous systems (Bailey, 1978, 1982) and information regarding aqueous ozonation has until recently been extremely limited.

The molecular and radical reactions of ozone with natural organic matter are also discussed by Glaze (1987). Briefly, he states that (1) free or complexed metals can be oxidized and will further participate in reactions, (2) ozone can react with aromatic moieties of humic material to produce phenolic groups which are made more susceptible to attack, (3) ozone can abstract hydrogen atoms from aliphatic side chains of fatty acids whereby the radicals formed will add molecular oxygen to form peroxides which decompose to superoxides and (4) ozone can react with carbon-carbon double bonds forming peroxidic intermediates which release hydrogen peroxide and leave carbonyl compounds. Aldehydes, carboxylic acids and aliphatic and aromatic mixed oxidized species generally result from such ozonation. While ambient concentrations of most of these by-products

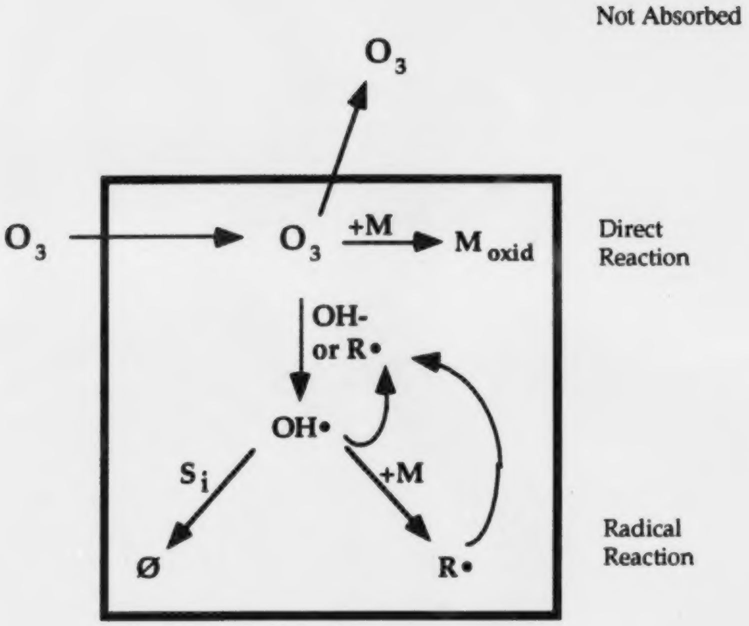


Figure 1.1 Ozone's Participation in Free Radical Reactions (O_3 = molecular ozone, M = substrate, M_{oxid} = oxidized substrate, OH- = hydroxide ion, OH· = hydroxyl radical, R· = organic radical, S_i = scavenger, Ø = end product; Adapted from Hoigné and Bader, 1983)

can be considered harmless, it was recognized that potentially harmful by-products simply may not have been detected by available analytical methods.

Bicarbonate ion scavenges free radical species and thereby promotes the molecular pathway. This has important implications with respect to drinking water treatment DBP production as the concentration of total carbonate species (which is often referred to in the drinking water treatment industry as alkalinity) varies from source to source. Reckhow, Singer and Legube (1986) found that small amounts of bicarbonate significantly improve trihalomethane precursor destruction by shifting the oxidation pathway away from the free radical toward the direct oxidation, or molecular, pathway (also in Legube *et al.*, 1985 and Doré *et al.*, 1987). These results are attributable to the selectivity of molecular ozone reactions with aromatic and unsaturated components of natural humic materials. Glaze (1986) stated that under drinking water treatment conditions, it is likely that the free radical pathway dominates; however consideration must be made of the individual source water bicarbonate concentration.

1.2 Organic By-Products of Ozonation

The subject of by-product identification from the aqueous ozonation of organic compounds is a relatively recent one: much of the early ozonation work involved non-aqueous solutions. This section of the literature review primarily reports on the aqueous ozonation by-products of specific organic compounds which are either components of natural organic matter (NOM) or are by-products of NOM oxidation.

A list of identified ozonation by-products was compiled by Mallevialle (1982) from available, but unreferenced literature. The table contains compounds which have been ozonated, with identifications of their corresponding by-products. Where applicable, compounds yielding measurable ozonation intermediates were identified along with the intermediates to which they corresponded. With regard to compound classes, the observations generally followed established trends. Alkanes and olefins were ozonated to alcohols or epoxides, then to aldehydes or ketones and finally to acids. Aromatic hydrocarbons produced phenols, hydroquinones and similar compounds which could subsequently be oxidized to acids. Aldehydes, ketones and carboxylic acids were similarly identified from the ozonation of humic acids, and oxalic acid was a common endproduct of the ozonation of a wide variety of organic compounds. Amino compounds typically produced nitrocompounds or inorganic nitrate on ozonation, whereas 4-Aminobenzoic acid produced ammonia and formic acid. Nitrogen heterocycles produced oxidized forms of the heterocycle. For example caffeine produced dimethylparabanic acid, N-methyloxalamide and N-N'-dimethyloxalamide, and quinoline produced nicotinic acid and quinolinic acid. Sulphides produced sulfoxides and sulphones on ozonation. The list published was not meant to be exhaustive but did give an indication of the results published to date.

Glaze (1988) reported that the compounds most likely to be formed upon ozonation of NOM during drinking water treatment are carboxylic acids, aldehydes, ketones, epoxides, phenols, quinones, furans and alcohols. While the classes of by-products can sometimes be predicted, only a few of the actual compounds have been identified, the most commonly reported ones being the low molecular weight aldehydes (for example, Krasner *et al.*, 1989; Huck *et al.*, 1989, 1990). However, the variability of by-products expected from ozonation of natural waters was also addressed, suggesting that generalizations are difficult to make. For example, ozone dose has a major impact, and the low dosages used for drinking water treatment will not likely produce the two-carbon by-products observed for high doses, but rather partially oxidized products would be expected. Unsaturated fatty acids commonly yielded aldehydes and carboxylic acids upon ozonation (formaldehyde, aldehydes detected as ranging in size from 6 to 10 carbons in length) with formaldehyde yields about ten times that of other aldehydes. Also formaldehyde, and perhaps other species, continued to be formed hours after ozonation was terminated complicating interpretation of results. It was also suggested that interest in by-products such as carboxylic acids was considered minimal from a health perspective but may be greater with regard to biotreatment technologies and distribution system stability.

1.2.1 Hydrocarbons

1.2.1.1 Alkanes, Alkenes, and Alkynes

The oxidation of hydrocarbons by ozone and other oxidants has been extensively studied and is reported in many texts (for example, Allinger *et al.*, 1976; Bailey, 1978). Free radical reactions occur with alkanes, alkenes and alkynes, and molecular ozonolysis is known for the unsaturated hydrocarbons, as described in Section 1.1.2. However, ozone does not react well with aliphatic compounds with electron withdrawing substituents (for example, organic halides), nor with aliphatic compounds in general unless they have easily oxidizable groups (aldehydes and ketones) (Glaze, 1987). With respect to applications to drinking water treatment, Singer (1988) found that oxidation of olefins by ozone leads to the formation of aldehydes. Also, Gauducheau *et al.* (1986) found that ozonation of citraconic acid ($HOOC\text{-}CH{=}C(CH_3)COOH$) lead to the formation of glyoxylic, acetic, formic, oxalic, pyruvic and hydroxypyruvic acids, the relative abundance of which depended on the initial reactant concentrations employed. Glyoxylic acid was identified as an important intermediate in these reactions.

1.2.1.2 Aromatic Compounds

Ozonation of aromatics is said to be slow unless activating functionalities such as hydroxyl or amino groups are present, and major products determined to date have been those due to ring cleavage as well as quinones, hydroquinones and aromatic aldehydes and acids (Glaze, 1986). In addition, Maggiolo (1978) has detected phenols. Hoigné (1982) and Hoigné and Bader (1983a, 1983b) determined the second order rate constants (which range over twelve orders of magnitude) for the reaction of molecular ozone with various organic compounds. Under drinking water treatment conditions, activated aromatics such as phenol and resorcinol, olefins and simple amines react quickly with molecular ozone. The free radical decomposition product of ozone (hydroxyl radical) reacts quickly and non-selectively (second order rate constants ranging over 2 - 3 orders of magnitude) with organics that are resistant to molecular ozonation such as aliphatic acids, aldehydes, ketones and less activated aromatics. High pH and ultraviolet irradiation promote ozone decomposition and enhance the free radical pathway while low pH and free radical scavengers such as bicarbonate favour the molecular ozone pathway.

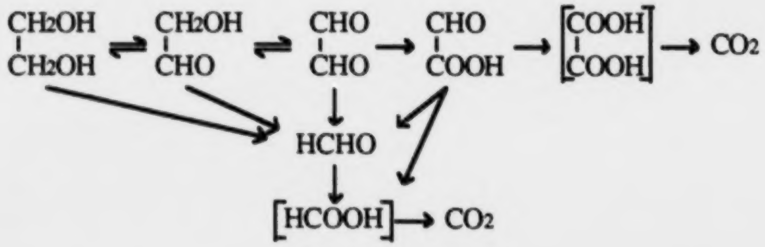
In addition, the ozonation of PAHs acenaphthylene and acenaphthene was reported by Chen *et al.* (1979). The major by-products found were 1-naphthoic acid, 1,8-naphthaldehydic acid, 1,8-naphthdialdehyde and 1-indanone-7-carboxylic acid, none of which appeared to have any inherent toxicity.

1.2.2 Oxygen-Containing Molecules

Ozone reacts with NOM to form a variety of oxygenated by-products. These compounds can then be further reacted with ozone to form secondary by-products. The following are a few examples of the aqueous ozonation of relatively small oxygenated molecules which might themselves be ozonation by-products of NOM.

1.2.2.1 Aldehydes, Acids, Ketones, Furans, Alcohols and Ethers

The reaction of ethylene glycol with ozone and ozone/electrolysis, as reported by Takahashi and Katsuki (1990), included kinetic data and by-products formed.



Glycoaldehyde, glyoxal, glyoxylic acid and formaldehyde were all identified reaction products, as shown in this reaction scheme. It was thought that removal through formation of formic acid was more prevalent than removal through the oxalic acid intermediate. The reaction order was 0.8 with respect to ethylene glycol concentration and 0.7 with respect to ozone concentration in the feed gas. Complete total organic carbon (TOC) removal could only be obtained by the ozone/electrolysis combination, for which it was thought that the increased efficiency was due to greatly increased free radical production during the ozone/electrolysis procedure. Oxalic acid was only observed when excess sodium carbonate was added to the reaction mixture, indicating a scavenging of free radicals.

Caprio *et al.* (1989) reported on the chemistry and kinetics of glyoxal ozonation. Glyoxal is a major ozonation product of benzene, naphthalene and 2-butenal (among other compounds) and is a substance which denatures native DNA of T2 phage by unwinding guanosine- and cytosine-rich regions of DNA (Broude and Budowsky, 1973). The reaction was first order in both reactants. Glyoxalic acid, oxalic acid and carbon dioxide were formed by a free radical mechanism in which molecular oxygen also participated. The following mechanism was proposed:

$$\mathrm{OHC\text{-}CHO} + \mathrm{O_3} \rightarrow \mathrm{OHC\text{-}\dot{C}O} + \cdot\mathrm{OH} + \mathrm{O_2}$$

$$\mathrm{OHC\text{-}CHO} + \cdot\mathrm{OH} \rightarrow \mathrm{OHC\text{-}\dot{C}O} + \mathrm{H_2O}$$

$$\cdot\mathrm{OH} + \mathrm{S_i} \rightarrow \text{Termination}$$

$$\mathrm{OHC\text{-}\dot{C}O} + \mathrm{O_3} \rightarrow \mathrm{OHC\text{-}COO}\cdot + \mathrm{O_2}$$

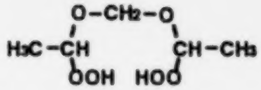
$$\mathrm{OHC\text{-}COO}\cdot + \mathrm{OHC\text{-}CHO} \rightarrow \mathrm{OHC\text{-}COOH} + \mathrm{OHC\text{-}\dot{C}O}$$

where S_i represents an hydroxyl radical scavenger. Comments on instability of peroxidic intermediates were offered.

Methylglyoxal is a product of ozonation of methylated benzenes which behaves similarly to retine and other alpha-ketoaldehydes which inhibit cell growth by reacting with sulfhydryl groups on DNA molecules (Basu *et al.*, 1988; Együd and Szent-Gyorgyi, 1966). Glutathione and glyoxalase I and II, however, were very efficient at degrading methylglyoxal compounds into lactic acid and associated alpha-hydroxy acids, especially at the concentrations expected in drinking water (maximally parts per billion or trillion).

Rice and Gomez-Taylor (1986) reported that aqueous ozonation resulted in formation of aldehydes, ketones, carboxylic acids and hydrogen peroxide. Oxalic acid (HOOC-COOH) was the end product of the ozonation of several aliphatic, aromatic and heterocyclic compounds, as was acetic acid. Formic acid and formaldehyde could be oxidized to carbon dioxide and water, whereas chlorinated materials underwent ozonation slowly (also reported by Glaze, 1987). Compounds unreactive to ozone included oxalic acid, acetic acid, glycerol, urea, saturated hydrocarbons, perlargonic acid, hexanoic acid, octanoic acid and the explosive 'RDX'. Amino acids reacted with ozone to form ammonium and nitrate ions without the formation of nitriles produced by chlorination. Alanine reacted readily while phenylalanine is more resistant and formed some polymeric material. In general, aromatic rings were hydroxylated in the first ozonation reaction step, followed by the production of quinones as initial intermediates. Phenols thus formed could be oxidatively coupled (especially under high pH, low ozone concentration conditions, also discussed in Chrostowski *et al.*, 1983), a phenomenon which may be responsible for microflocculation. Ozonation of either phenol or aniline resulted in formation of resorcinol, a known THM precursor. In addition, ozone reacted with chlorinated pesticides to form more toxic intermediates (for example, parathion yielded paraoxon) or intermediates resistant to further ozonation (for example, heptachlor epoxide).

Several model compounds were ozonated by Spanggord and McClurg (1978). The reaction products were evaluated by Ames testing and, if found to be biologically active, were subjected to chemical analysis for identification. Oleic acid ($C_{18}H_{34}O_2$) produced classical ozonation products, primarily by the molecular mechanism. Ozonide or epoxidic intermediates were not observed and it was suggested that they would not have survived at the reaction pH of 3.8. Ethanol produced acetic acid and acetaldehyde as expected and previously observed. Formaldehyde was also observed. Evidence also suggested that hydrogen peroxide and alkyl hydroperoxides were present in that oxygen was liberated on reaction with lead tetraacetate. As well, the compound shown following was formed.

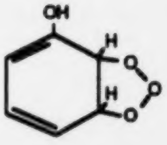


This compound appeared to be formed by the condensation of acetaldehyde, formaldehyde and hydrogen peroxide, indicating that formaldehyde and acetaldehyde were not necessarily end products of the reaction.

1.2.2.2 Phenols

Ozonation of phenol has been extensively studied in both drinking water and wastewater. Products of phenol ozonation include resorcinol, catechol, hydroquinone, cis-cis muconic acid, glyoxylic acid, glyoxal, oxalic acid, formic acid and formaldehyde (Eisenhauer, 1968, 1971; Gould and Weber, 1976; Yamamoto *et al.*, 1979; Doré *et al.*, 1980; Singer and Gurol, 1983).

Spanggord and McClurg (1978) found that ozonation of phenol produced catechol and resorcinol, as has been observed by others. A reactive intermediate (shown below) was postulated which could explain the formation of either product by the elimination of oxygen. However, Maggiolo (1978) found that phenol ozonation proceeds quickly by the hydroxyl free radical pathway, and that much lower ozone concentrations were required when performed at pH 12 than pH 7 due to the formation and reaction of hydroxyl radicals.



Gauducheau *et al.* (1986) studied the ozonation of *o*-chlorophenol and found that the products observed depended on the concentrations of reactants employed. Higher initial concentrations of reactants produced fewer end products. They also noted that as the ozonation progressed the solutions became slightly coloured, which was indicative of formation of hydroxylated aromatic or quinonoid compounds.

Wang (1990) found that anaerobic biodegradation of by-products from the ozonation of o-cresol, benzenesulfonic acid, 2,5-dichlorophenol and 2,4-dinitrophenol proceeded to complete mineralization to methane. Ozonation reduced the toxicity of 2,5-dichlorophenol and 2,4-dinitrophenol, and ozonation at high pH produced the most beneficial effects. Ozonation by-products identified included acids (formic, acetic, propionic, glyoxylic, oxalic and salicylic) and phenol.

1.2.3 Nitrogen-Containing Molecules

There is little in the literature regarding ozonation of nitrogen-containing organics despite their occurrence in natural matter. Granted, elemental analyses of humic and fulvic material generally shows that the nitrogen content is small (of the order of 1-6 %; Aiken *et al.*, 1985) compared with the carbon, hydrogen and oxygen contents (approximately 50, 4 and 40%; Aiken *et al.*, 1985). However, nitrogenous material is significant in aqueous systems; amino acids, purines and pyrimidines have all been isolated from such sources (Ram and Morris, 1980), some of which have been shown to produce carcinogenic nitrosamines (Magee *et al.*, 1980), nitroaromatics and heterocyclics upon chlorination and which may react similarly on ozonation. In addition, Jolley and Carpenter (1983) suggest that concentrations of organic amines in surface waters and some groundwaters may be much greater than ammonia concentrations, possibly affecting toxicity of chlorine-treated water.

1.2.3.1 Amino Compounds

In non-aqueous solution, simple (non-heterocyclic) amines yield nitro-compounds, nitroxides and products from attack on the carbon chain (Oehlschlaeger, 1978). At the time of writing, little work had been done on the aqueous ozonation of amines, but it was hypothesized that it would likely involve reaction of the carbon side chains rather that the nitrogen since salt formation in aqueous solution causes unavailability of the nitrogen electron pair to electroplilic ozone attack.

Several model nitrogenous compounds were ozonated by Spanggord and McClurg (1978). The reaction products were evaluated by Ames testing and, if found to be biologically active, were subjected to chemical analysis for identification. Diethylamine produced three products, acetaldoxime and two similar structures. Several tertiary nitrogenous compounds incorporated 16 mass units into their structure on ozonation, indicative of the formation of amine oxides. Such amine oxide formation has also been reported by others (for example, Falk and Moyer, 1978). Caffeine is one example of such a compound. In the case of diphenylhydrazine, data suggested that the oxygen could be incorporated into the aromatic ring depending on the reaction pH (at low pH, the amine functional group would be expected to be protonated and therefore non-reactive). With regard to amino acids reactions, Spanggord and McClurg (1978) found that reaction of ozone with glycine produced a compound that resulted from ozone attack at both the nitrogen and the alpha carbon. Amides, however, were resistant to ozonation (Falk and Moyer, 1978).

1.2.3.2 Nitro Compounds

Xu *et al.* (1989) studied the ozonation in combination with ultraviolet (UV) irradiation of three nitrogen-containing compounds: o-nitrotoluene, p-nitrotoluene-2-sulfonic acid and p-methylaniline-3-sulfonic acid. pH manipulation was utilized mid-treatment to reduce carbonate and bicarbonate species (radical scavengers) and improve removal efficiencies. Specific by-products were not identified, although treatment of formic and acetic acid was performed to address continued ozonation of expected by-products. In this latter part of the experiment, a pH effect opposite to that expected was observed (more analyte reduction at low pH than at high pH). It was suggested that hydroxyl radicals (·OH) reacted with acetic acid (CH_3COOH) to form $\cdot CH_2COO^-$ and $\cdot OOCH_2COO^-$ secondary radicals which did not react further with ozone. It was also suggested that the inhibiting effect of $\cdot CH_2COO$- was counteracted by promotional effects of ozone decomposition accelerated by UV irradiation.

Baozhen and Jun (1988) studied the ozonation of five aromatic nitro-compounds; p-nitroaniline, nitrobenzene, p-dinitrobenzene, p-nitrotoluene and m-dinitrobenzene. They found that the above order represented increasing difficulty in oxidation. Concentrations studied were 10-20 mg/L and detection of substrate removal was by UV spectrophotometry (approximately 375, 265, 265, 280, 240 nm, respectively). Removal was found to be first order in all cases. Some products which were consistently formed typically had UV absorbances of 200-230 nm, representing nitro groups (nitrite and nitrate ion) stripped from the aromatic rings. Various pHs between 2 and 11 were examined. Explanation of the order of susceptibility was given below:

> "Since the attack of ozone is electrophilic, it generally occurs on the site with the denser aromatic ring electronic cloud. Therefore, the more nitro groups, the more difficult the attack of ozone. With regard to the reactivity to ozonation, nitrobenzene > dinitrobenzenes, for different species of dinitrobenzenes, the para-substituting nitro group is more susceptible to ozonation compared with the meta-substituting nitro group. Both methyl and amino groups are ortho- or para-orienting groups with electronation, causing an increase in electronic cloud density, and thus leading to activation of the aromatic ring, which is susceptible to electrophilic attack. Moreover, when two substituting groups are present, the ozonation attack is directed predominantly by the para-orienting group. Since the amino group is a type of strong ortho-orienting group (its orienting ability is much greater than that of the methyl group), nitroaniline is more susceptible to ozonation, - compared with nitrobenzene and p-nitrotoluene. The methyl group of p-nitrotoluene exhibits weak orienting ability, and its orienting effect is comparable to that of a nitro group, thus enabling the p-nitrotoluene to be more difficult to degrade by ozonation in comparison with amino-substituted aromatic hydrocarbons."

Gould (1987) reported on some preliminary observations of correlations between ozonation kinetics and chemical structure as defined by Linear Free Energy Relationships. First order rate constants correlate well with Hammett Polar Constants and, for 2-alkyl-4,6-dinitrophenols, the Steric Parameter. Reaction rates increased with increasing electron density in the aromatic ring and decreased with increasing size of alkyl substituent. The compounds studied were a series of 2-alkyl-4,6-dinitrophenols, three substituted pyrimidines and several substituted phenols.

1.2.3.3 Carbamates, Amino Acids

The reaction of ozone with carbamate pesticides has been studied by Mason *et al.* (1990). Carbamates are esters of carbamic acid (NH_2COOH) in which the oxygen and nitrogen atoms have aliphatic or aromatic substituents. They are more biodegradable than organochlorine pesticides and although less toxic to mammals than organophosphates, their solubility and stability under certain conditions makes them dangerous in drinking water. Some metabolites of aldicarb are toxic and aldicarb sulfoxide was identified as a product of its ozonation. For aromatic carbamates such as propoxur, hydrolysis and ring hydroxylation occur.

1.2.3.4 Heterocycles

N-Heterocyclic compounds form the building blocks for DNA and so are ubiquitous in the environment. Similarly, in plants, all indole alkaloid N-heterocycles are originally derived from tryptophan by way of tryptamine (Allinger *et al.*, 1976).

Oehlschlaeger (1978) surveyed the reactions of ozone and several classes of compounds. Except for pyridine, most aromatic heterocyclics compounds were readily attacked by ozone. In general, the aromatic ring was usually the site of attack to produce aromatic aldehydic and acidic derivatives. For example, quinoline reacted to produce nicotinic acid in good yield. Simple heterocyclics (pyroles and furans) yielded formic and acetic acids (furans) and amines or ammonia (pyroles).

5-Chlorouracil is a compound isolated from the chlorination of uracil in natural waters. It is structurally and functionally similarly to thymine, an important constituent of DNA, and hydrolyzes in water under photolytic conditions (Southworth and Gehrs, 1976). The first step involves hydration of the 5-6 double bond. Dechlorination follows, then formation and rapid degradation of barbituric acid and isobarbituric acid, neither of which is chromophoric.

Shapiro *et al.* (1978) reported on the ozonation products of caffeine, a major component of the effluent from a sewage treatment facility (Upper Thompson). Typical concentrations are on the order of 1 mg/L, but experiments were conducted at 660 mg/L to alleviate analytical sensitivity problems. Four major and four minor products were identified. Of large abundance was dimethylparabanic acid (34 %), which had previously reported as an oxidation product of caffeine, and has been found to be non-mutagenic by the Ames test (Ames 1975, 1976 in Shapiro *et al.*, 1978). Of lesser abundance was N,N'-dimethyloxalamide (1-2%) and other compounds of uncertain structure, one of which constituted 44 % of the total product abundance and had a molecular weight of 198.

Triphenylmethane colouring agents such as 'Basic Violet 14' were found to fade on ozone application (Grosjean *et al.*, 1989) and some reaction by-products were identified (substituted benzophenones such as methyldiamino- and diaminobenzophenone, phthalimide, aminobenzoic acid, benzoic acid, benzoquinone, benzaldehyde and phenol) indicating that ozone was adding to the double bond under the conditions studied (atmospheric contact).

Legube *et al.* (1987) reported on the ozonation products of four nitrogen heterocycles - amitrole, atrazine, 1-methylbenzotriazole and 5-methylbenzotriazole. Ozonation was performed at slightly acidic pH (4.7-5.5) (therefore favouring molecular reaction) using ~0.1 mM reactant and ~2-25 mmol ozone/mol reactant (ozone demand of

~2.5 mmol/mol), and analysis was by reverse phase high performance liquid chromatography. Methylated isolates were analyzed by gas chromatography with mass spectral detection. Various types of ozonation by-products were identified, involving both intact and broken aromatic rings. Ozone did not open atrazine's six membered ring while it did break the five membered ring of amitrole (and of the triazoles) to form carbamic acid and formamide, among other products. This effect had been previously observed by Doré (1984 in Legube *et al.*, 1987). Duguet *et al.* (1990) described in a research note that while 46% reductions in atrazine concentration were possible with ozone alone, the removal increased to 89% using an ozone/hydrogen peroxide system (by-products were not mentioned, and the article stated that further work was scheduled to be published soon).

Erb *et al.* (1979) also studied the ozonation of atrazine in water but found that reaction would occur only in very pure water. She postulated that humic material in raw water protected the pesticide from ozone attack. By-products were not identified in the study.

1.3 Reactions of Ozone with Humic and Fulvic Materials

1.3.1 Humic Content Overview

Natural organic matter (NOM), both aquatic and terrestrial, represents a considerable portion of both the building blocks and end products of life processes and is ubiquitous. The NOM from surface waters has been classed into the general constituents shown in Figure 1.2 (Malcolm, 1991). Approximately half of this material is made up of humic and fulvic acids, present in a 1:9 mass ratio. Humic and fulvic acids are operationally defined such that fulvic acids remain soluble at pH 1 or less, whereas humic acids form precipitates under these conditions. Both of these classes of NOM are highly coloured and several hypothetical structures have been proposed which include various chromophoric groups. Three of these are illustrated in Figures 1.3 to 1.5. That shown in Figure 1.3 is among the earlier attempts at deducing the structural components of this

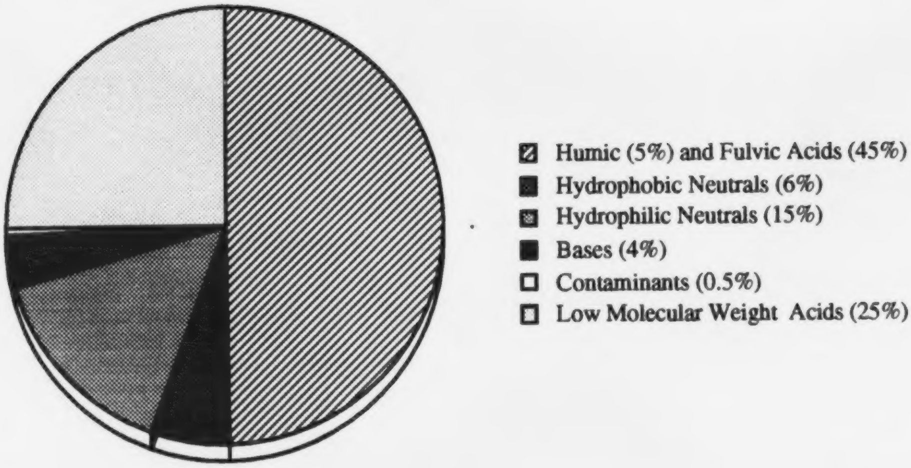


Figure 1.2 Distribution of Surface Water Dissolved Organic Carbon in Rivers of the United States (Adapted from Malcolm, 1991)

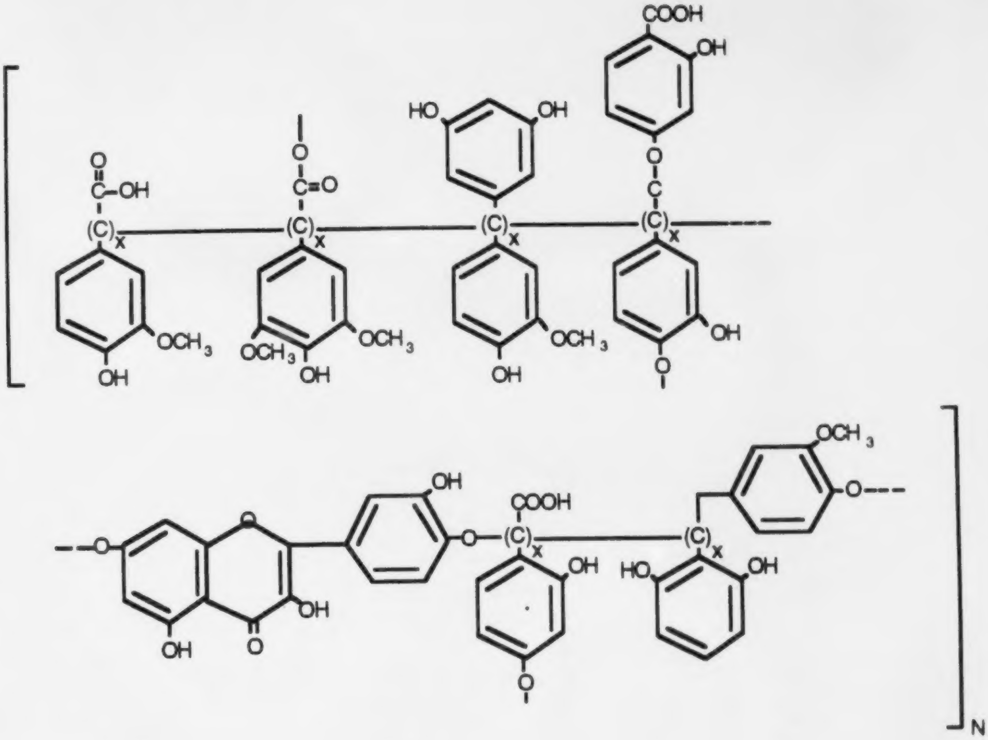


Figure 1.3 Proposed Structure of Colour Macromolecule (Adapted from Christman and Ghassemi, 1966)

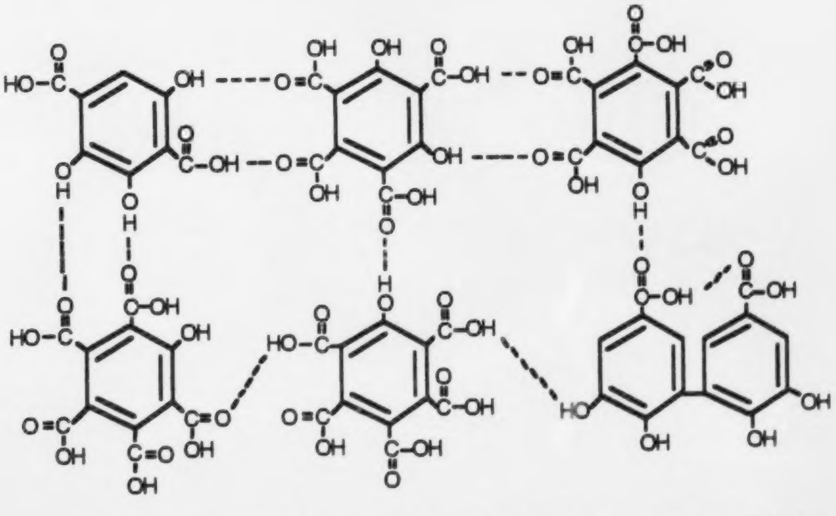


Figure 1.4 Suggested Chemical Structure of Fulvic Acid (Adapted from Schnitzer and Khan, 1972)

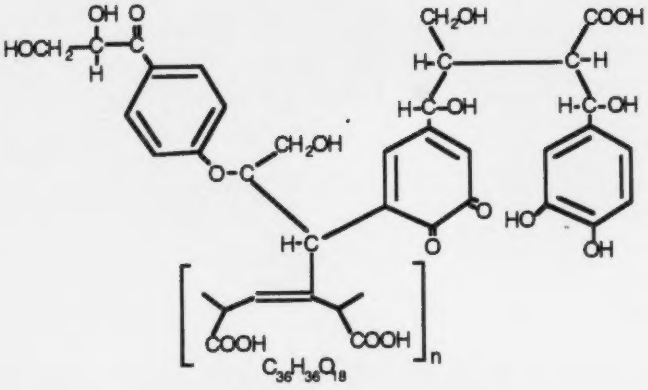


Figure 1.5 Proposed Tetramer Structure for Humic Acid (Adapted from Steelink, 1985)

macromolecular material. Structures which have been proposed more recently contain many of the same components but are based on investigations using newer technology (Figures 1.4 and 1.5). Similar advances in structural determinations have been further updated by Hayes *et al.* (1989b; although proposed structures were not illustrated).

The NOM constituting humus has been divided into several subclasses, the exact definitions of which vary with the operational or other conditions under which they are studied. It is extremely heterogeneous and complex, being composed of substances ranging in molecular weight from less than 100 daltons to much greater than 5000 daltons (up to or exceeding 100,000 daltons). While agricultural and geological interests have always provided an impetus for the study of terrestrial NOM, issues such as the discovery of disinfection by-product formation in drinking water treatment have increased the interest in aquatic NOM in recent years, or at least provided another area of research to which its study can be applied (that of drinking water treatment).

Because of their high colour content and abundance, and because methods for their isolation are available, much research has involved the use of these NOM fractions. The choice of NOM isolation method adds another modifier to the operational definition of humic and fulvic acids described above in that isolation of different portions of the humus will be either enhanced or reduced depending on the method used. The most common means to isolate aquatic humic and fulvic acids in North America has been by adsorption onto non-polar polymeric resins such as Amberlite® XAD-8 (a methyl methacrylate polymer) and is the method of choice for the International Humic Substances Society (IHSS; Thurman and Malcolm, 1981; APHA-AWWA-WEF, 1992). Acidic functional groups in these molecules are protonated by acidification to pH 2, and the neutral molecule is then adsorbed. Limitations of this particular method of isolation are as follows. For example, some non-humic material can be co-adsorbed, particularly that which is hydrophobic or aromatic, and XAD-resins exhibit size exclusion characteristics such that the largest of the humic acid molecules may not be concentrated on these resins. Also, some humic material may irreversibly form aggregates at low pH and become trapped within the porous structure of the resin. Town and Powell (1993) found that some colour remained on the resins following desorption, possibly because of this phenomenon. They also found that while isolated coloured material was completely soluble at pH 3.6, acidification to pH 2.0 resulted in 60 % precipitation of this material. In studying the molecular size of the isolated and source materials, they found that the isolated humic materials contained more higher molecular weight components than did the source water, while the fulvic acids contained more lower molecular weight components than did the source water. It was thought that some aggregation occurred either during the preconcentration or precipitation (pH 1) steps of the isolation procedure. Despite these limitations, the XAD isolation method provides a high capacity, economical and reproducible means of isolating aquatic humus, and remains the current method of choice for the isolation of aquatic NOM.

The following review provides a brief discussion of aspects of humic and fulvic material relevant to drinking water treatment reactions. For further information, the reader is directed to two comprehensive reviews edited by Aiken *et al.* (1985) and Hayes *et al.* (1989a), which provide a strong basis for the study of NOM isolation, structure and chemistry. The earlier volume discusses humic geochemistry and means by which humic material can be isolated and characterized (for example, by elemental analysis, molecular weight determinations, and by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy). The latter review updates the first by providing information on newer techniques available such as electron spin resonance (ESR) spectroscopy, solid and liquid state ^{13}C NMR, electrophoresis and on the use of derivatization and degradation reactions in determining humic structure. Information presented in the following has been taken from these reviews in addition to the journal articles and conference proceedings cited.

1.3.2 Known Reaction By-Products

Application of ozone for the preparation of drinking water results in the formation of unwanted by-products through its reaction with aquatic natural organic matter (NOM), primarily of humic or algal origin.

Studies of the reaction of ozone with humic and algal matter indicate that within these macromolecules the overall effect of ozone on humic material is probably not to destroy the polymer but rather to oxidize part of its functional groups by attacking carbon-carbon double bonds, aromatic rings containing phenolic activating groups, and complexed metals such as iron (Glaze, 1986). Humic matter can also act as free radical reaction initiators, generating radical intermediates to further react in non-selective radical reactions to, for example hydroxylate benzene rings otherwise thought to be unreactive. Further reaction yields the aldehydes and acids mentioned previously. In water treatment, the nature of by-products generated by ozonation of humic material will vary with the nature of the humic material and the nature of the water (for example, with total carbonate concentration, also known as alkalinity). Most ozonation reactions in water treatment are ozone limited (low ozone to carbon ratios) and oxidation of macromolecular humic material does not generally result in many ring cleavage products but rather produces material which is more hydroxylated and polar than the initial material. Anderson *et al.* (1986a) show that O_3:C ratios up to 0.5:1 mineralize only about 35% of fulvic acid extracts to carbon dioxide and convert large molecular weight material to smaller molecular weight material. As well, Duguet *et al.* (1986, 1987) show that at low ratios oxidative coupling of phenol takes place to produce polymeric material.

Glaze (1986) shows that partial oxidation of humic material by ozone used at dosages typical of water treatment is difficult to detect spectroscopically. He states that three classes of ozonation by-products may be of health concern - organic peroxides (from olefins and aromatics, generally unstable in water but may be persistent depending on the organic moiety associated with the peroxide), unsaturated aldehydes (from polyunsaturated aliphatic or aromatic compounds, hepatotoxic) and epoxides (from olefins and aromatic compounds (limited) and unsaturated organics (in nonaqueous solvents), potential carcinogens.

Anderson *et al.* (1986a) studied the reaction of ozone with aquatic fulvic acids using Amberlite® XAD-8 chromatography and monitoring reaction products by ultraviolet (UV) spectrophotometry (254, 465, 665 nm). Studies were performed at neutral pH and ozone consumption was measured in addition to the above. It was generally found that there was a degradation of double bonds and oxidation of hydroxyl and amino chromophores such that ozone probably reacts first with the chromophores. Large molecular weight compounds were cleaved into smaller molecular weight compounds as measured by relative peak areas of the three peaks observed in the XAD-8 chromatograms. Finally, on a percentage basis, less TOC was removed by ozonation than UV.

Ozone oxidizes large molecular weight NOM to smaller molecular weight NOM. Using NOM fractionated by molecular weight, Owen *et al.* (1990) showed that ozone oxidized a portion of the NOM having greater than 5000 daltons to that having less than 1000 daltons. They also found that removal of NOM by coagulation was more efficient for the higher molecular weight fractions (greater than 1000 daltons).

With regard to DBP production, Coleman *et al.* (1992) utilized high concentrations (1 g/L) of a commercial humic acid to determine the effect of ozone dose on DBP formation. Ketones, aldehydes and carboxylic acids of two to five carbon lengths were formed for ozone dosages between 1:1 and 3:1 ozone:DOC ratios (mass basis). Carboxylic acids concentrations increased when ozone was applied at a 1:1 ratio, but decreased when it was increased to 2:1 and remained constant with further increases in dose. However, aldehyde concentrations, including those for glyoxal and methyl glyoxal, increased with increasing ozone dose for each of the doses attempted.

Killops (1986) studied the ozonation of humic and fulvic acids from river water and found that ozonation both generated organic by-products and released smaller molecules trapped within the macromolecular structure of the humic acid. Ozonation of the humic acids resulted in less than a 10 % increase in volatile material (although yields may have been reduced depending on the extraction efficiency of the Amberlite® XAD-2 resin used to isolate them). Analysis of these by-products indicated the presence of carboxyl groups, possibly as carboxylic acids. Individual carboxylic acids and some aldehydes were identified. Ozonation reduced the quantity of alkylnaphthalenes and there was an increase in the ratio of aliphatic material to aromatic material, as indicated by ^{1}H NMR measurements, indicating degradation of some of the aromatic structures. In addition, substantial colour reduction could be achieved even with ozone dosages of less than 3:1 mg:mg ozone:humic acid without significant chemical alteration of the bulk material. An observed increase in alkanes on ozonation, compounds not expected to be ozonation by-products, suggested that these compounds had been trapped within the humic macromolecule and released on ozonation. Changes in pH were also suspected to be capable of causing similar release of trapped components. Raw water characteristics and seasonal variations were stressed for application of this data to other situations.

The effects of ozone concentration, UV intensity and reaction temperature on the kinetics of the removal of THM and total organic halide (TOX) precursors by ozone-UV was studied by Kusakabe *et al.* (1990). Experiments were conducted at pH 6.9 (phosphate buffer controlled) using humic acid solutions (NVDOC approximately 100 mg/L) and a 4 cm ID x 25 cm reaction column. Residual ozone was quenched with sodium sulfite which may have removed some of the more reactive by-products. Ozone concentrations were between 0.2 and 0.4 mol/m^3. Humic acid molecular weight fractions were determined by a gel permeation chromatograph with Tosoh G4000SW column. Ozonation by-products were determined by high performance liquid chromatography (HPLC) with UV detection (Shodex Ionpact C-811 column, eluant 0.1% phosphoric acid). Chlorination was performed at about 80 mg/L chlorine per 10 mg/L NVDOC at 20 °C for 24 h. Not unexpectedly, humic acid decomposition was much faster (approx. 100 times) in the presence of UV irradiation. The ratio of carbon dioxide released by NVDOC to ozone consumed was 0.4 to 0.6. Molecular weight distribution following ozonation of humic acid appears to be a bimodal function (Figure 1.6) - initial molecular weights of about 3000-5000 are oxidized to molecular weights of about 200-400.

Xiong *et al.* (1992) showed that ozone consumption increases with increases in ozone dose, pH and the degree of colour for several isolated fulvic acids. This overall consumption was even higher in the absence of radical scavengers such as carbonate species. Hydrogen peroxide and glyoxylic acid were identified as precursors of radical chain reactions.

1.4 Algogenic Material

1.4.1 Overview

Algogenic material, as the name suggests, is that part of the natural organic matter which is derived from algae, either directly from the algal cells themselves or as extracellular organic matter (EOM) secreted by the cells. Algogenic EOM is very polar and largely aliphatic, with little or no aromatic content, and has considerable polysaccharidic character. EOM is composed of several polar compound classes, including for example glycols, glycoses, deoxyglycoses, glyconic acids, glycuronic acids and glycaric acids (Hoyer *et al.*, 1985). Neutral and acidic polysaccharides typically constitute 20 to 40 % of the EOM, whereas uronic acids make up approximately 2 to 10 % of the EOM. The exact composition and properties of EOM depend both on the species being studied and its growth phase (Hoyer *et al.*, 1985, 1987). EOM is typically released from algae under light- or nutrient-limited conditions, and when cultures are in a declining growth phase (which includes EOM from cell autolysis, decomposition). The molecular weight of the bulk of algal EOM is less than 2000 daltons for most spescies, although some species such as *Dictyosphaerium* produce EOM of much higher molecular weight.

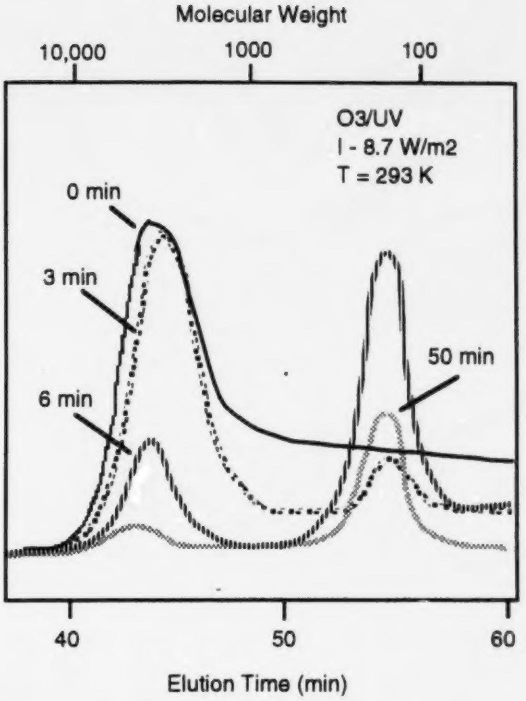


Figure 1.6 Change in Molecular Weight Distribution on Ozonation (Adapted from: Kusakabe *et al.*, 1990)

In addition, some components of EOM are toxic to other organisms. For example, two types of cyanobacterial toxins include the microcystins, which are cyclic heptapeptides, and the anatoxin-a toxins, which are alkaloids (Feuillade, 1992).

Palmer (1980) describes the role of algae in several different types of water. In terms of treatment for drinking water, minimal impact of algae would be observed for river water while significant effects would be expected for standing waters. As such, the effects of ozonation in each case (effects on flocculation, by-products) would be different and need to be studied individually.

1.4.2 Effects of Ozonation

Hoyer *et al.*, (1987) found that in addition to humic matter, algogenic matter (EOM) can be an important water constituent affecting drinking water treatment effectiveness, especially for surface waters. They used both isolated EOM and alginic acid (as a model compound) to determine why ozone sometimes impairs rather than enhances flocculation. Because algogenic EOM does not have an appreciable aromatic component, ozone did not act to increase the amount of carboxylic acid (COOH) groups on the surface of polysaccharidic EOM (which occurs with humic acid). Rather, ozone first degraded the EOM to monomers (without COOH groups), then further oxidized the monomers to COOH groups which impaired flocculation. Therefore, they recommend that overdosing of ozone be avoided if microflocculation is desired.

The phenomenon was further complicated by the observation that an opposite effect could result depending on the species of algae present (Hoyer *et al.*, 1987). Predominant species in the North Saskatchewan River are described by Anderson *et al.* (1986b), and those in Driedmeat Lake are given by Allen (1989) and Mitchell and Prepas (1990). However, flocculation performance in algae-containing waters can be predicted by determining the coagulant polymer acidity in the presence of the algae as outlined in Horn and Heuck (1983).

1.5 Chlorination and Chloramination By-Products of Humic/Fulvic Acids

Adoption of ozone in drinking water treatment will not likely result in the total elimination of halogenated disinfection by-products (XDBPs) associated with chlorine use. Even if ozone is adopted as the disinfectant of choice for primary drinking water disinfection in North America, it is not likely to be used as a sole disinfectant because of its short-lived residual and the potential for bacterial regrowth in the distribution system. A secondary disinfectant, either chlorine or chloramines, will be required to maintain the stability of treated water in the distribution system. Use of ozone prior to these secondary disinfectants may or may not alter the types and/or quantities of XDBPs formed from natural organic matter (NOM), of which approximately 50 % are made up of humic and fulvic acids.

Reactions of chlorine and, to a lesser extent, chloramine with humic and fulvic acid have been studied extensively and are reported in several reviews and conference proceedings (for example, Jolley *et al.*, 1978 to 1990; Christman *et al.*, 1990; Kanniganti *et al.*, 1992; Reckhow and Singer, 1990). Chlorination of this NOM leads to the production of several classes of XDBPs, among which the trihalomethanes (THMs) have been the subject of the greatest amount of study. However, the effects of ozonation and subsequent chlorination or associated water treatment processes on the production of these XDBPs is also a subject of relatively recent study, and forms the basis for the following review. Also, while the chlorination of humic and fulvic acids has been studied in great detail, other NOM fractions (Figure 1.2) remain relatively unexplored as to their XDBP precursor potential.

Not included herein are specific references to the formation of brominated XDBPs which have been identified in disinfected waters containing high bromide ion concentrations. This topic is discussed or reported by others (Cavanagh *et al.*, 1992; Symons *et al.*, 1993; Siddiqui and Amy, 1993; Krasner *et al.*, 1993; Pourmoghaddas *et al.*, 1993; Summers *et al.*, 1993; Glaze *et al.*, 1993; Coleman *et al.*, 1992)

The effect of ozonation on chlorine demand has been recently investigated either directly or indirectly by several researchers. In studies using isolated fulvic acids as the NOM model, the presence or absence of alkalinity has been shown to influence chlorine demand. Jadas-Hécart *et al.* (1990) and Paillard *et al.* (1989) found that ozonation increased the chlorine demand of the fulvic acid in the absence of alkalinity and that higher dosages produces greater increases in chlorine demand; however, the opposite effect was observed when alkalinity was present at 180 mg/L as calcium carbonate. In the latter case, ozonation decreased the chlorine demand of the fulvic acid, and the effect was only observed for ozone dosages of less than or equal to 0.5 mg ozone:mg fulvic acid. Paillard *et al.* (1989) also determined some XDBPs in their study: chloroform ($CHCl_3$), trichloroacetic acid (TCAA) and dichloroacetic acid (DCAA). The overall effect of ozone was to reduce the concentrations of XDBP precursors, except for that of dichloroacetic acid (when ozonated without added alkalinity). They also found that the presence of alkalinity improved the extent to which ozonation reduced XDBP formation.

Owen *et al.* (1990) found that ozonation of various molecular weight NOM fractions with ozone doses of between 0.8 and 1.0 mg ozone:mg carbon removed approximately 30 % of the haloacetic acid and haloacetonitrile precursors. They also observed that the majority of the XDBPs formed were associated with the lower molecular weight NOM fractions (less than 1000 daltons). This was also observed by Schnoor *et al.* (1979) and is significant because many of the early studies on XDBP production involved the use of humic acids of much higher molecular weight.

In an early study by Kuo *et al.* (1977), small organic compounds which were known or expected to be products of the ozonation of fulvic acid were ozonated and chlorinated to identify the final by-products formed. These included 2-propanol, acetic acid and oxalic acid. Halogenated DBPs identified were the trihalomethanes and some halogenated alkanes, and the effect of ozonation was to reduce their concentrations. The authors acknowledge that some of this reduction may have been from stripping of the precursor materials during ozonation, as well as from precursor oxidation.

Yamada *et al.* (1986) ozonated and then chlorinated several precursor materials expected to be of similar composition to humic acid and showed that high doses of ozone (greater than 8 mg:mg carbon) reduced the concentrations of trihalomethanes. Actually, both increases and decreases in XDBP production were observed. According to their findings, aliphatic compounds containing carbonyl groups, an expected result of the ozonation of aromatic moieties, were not significant precursors for trihalomethanes. The major trihalomethane precursors were those which retained some aromaticity following ozonation. According to this data, low ozone dosages might be expected to increase the quantities of trihalomethane precursors while higher dosages would reduce them.

Coleman *et al.* (1992) utilized large concentrations of humic acids (1 g/L) to investigate the effects of ozonation on subsequent XDBP production. They found that ozonation at a 3:1 ozone:carbon dose reduced chloroform production by 59 % relative to that observed at a 1:1 ozone dose. Other XDBPs were similarly reduced at the 3:1 dose.

Other researchers have found that ozone has a variable effect on XDBP production, depending on the type of XDBP being studied and other factors. For example, when Black Lake fulvic acid was ozonated at various doses up to a 3:1 mass ratio of ozone:TOC prior to being chlorinated, decreases in chloroform, trichloroacetic acid and dichloroacetonitrile concentrations were observed relative to those of the non-ozonated material (Reckhow and Singer, 1984). However, ozonation did not affect the formation of dichloroacetic acid, and actually increased the concentration of trichloroacetone.

The complex nature and interrelatedness of the reactions involved in XDBP formation were studied by Reckhow and Singer (1984) who suggested that a common precursor material may exist for chloroform and trichloroacetic acid. Chloral hydrate proved to be insufficiently reactive to be that precursor, but syringaldehyde and pyruvic acid both produced chloroform and trichloroacetic acid similarly to that produced by humic materials. Ozone was shown to remove XDBP precursors in the order dichloroacetonitrile $>$ TCAA $\geq$ $CHCl_3$ $\geq$ TOX $>$ DCAA $>$ trichloroacetone, which agreed with a conceptualized model for the chlorination of humic acid. They later showed that XDBP yields obtained from the chlorination of natural water were similar to those obtained from the chlorination of isolated aquatic humic substances (Reckhow and Singer, 1990). These XDBPs included selected haloacetic acids, haloacetonitriles and trihalomethanes. The XDBP precursors were effectively removed by coagulation (greater than 60% removal), and ozonation decreased trichloroacetic acid concentrations but not dichloroacetic acid concentrations.

More recently, Speitel *et al.* (1992) ozonated and chlorinated two lakewaters and determined the effects of ozonation on subsequent formation of trihalomethanes and haloacetic acids. The results obtained varied with the source water used and the ozone dosage applied. Trihalomethane precursors in Lake Austin water were reduced by ozonation at dosages up to 5:1 ozone:TOC. In water from Lake Houston there was an initial decrease in precursor material, which reversed and showed increases in trihalomethane precursor formation at dosages above 3:1 ozone:TOC. The trend for formation of haloacetic acids in Lake Austin water was similar to that observed for trihalomethanes formation in Lake Houston water (an initial decrease followed by an increase, primarily in dichloroacetic acid). This same effect was also observed by Doré *et al.* (1988). Haloacetic acid formation in Lake Houston water decreased for ozone dosages up to 3:1 ozone:TOC and remained constant for further increases in ozone dose.

All of the above studies illustrate the complex nature of the reactions of aquatic NOM with chlorine, especially when ozonation is employed prior to chlorination.

1.6 Analytical Methods for Known and Expected By-Products

The comprehensiveness of studies on disinfection by-product (DBP) formation and control are limited by the choices of DBPs included, which can be a function of readily available technology or methodology for their analysis. With the discovery of trihalomethanes (THMs) in drinking water, many methods were developed for halogenated compounds known or suspected to be DBPs in order to account for a greater proportion of the DBPs formed. These methods continue to be updated (Hites and Budde, 1991). When studies incorporated these new halogenated DBPs into their experimental protocol, discrepancies in recommendations made regarding treatment control strategies became evident. For example, treatments to remove THMs were not as effective at removing other DBPs. Since DBPs resulting from non-chlorine-based disinfectants are a relatively new issue in drinking water treatment, at the time of writing there were gaps in the number of established methods available for these DBPs in drinking water. Therefore, in order to be more comprehensive in studying DBP production from ozonation in drinking water treatment, methods are being sought to determine as many of the expected DBPs as possible. These would include such compound classes as aldehydes, ketones, carboxylic acids, phenols and mixed functional group compounds such as the oxoacids.

In September 1989, the American Water Works Association published a comprehensive assessment of methods available for the analysis of polar organics such as those expected to be drinking water ozonation by-products (Sheldon and Smith, 1989). Considered were techniques for concentrating samples as well as instrumental analytical techniques. For example, Glaze (1987) suggests that some reports showing that ozone eliminates THMs may be erroneous, saying that sparging during sample preconcentration may be the mechanism of removal rather than chemical reaction. Singer (1990) also reported that methodology was generally found lacking for polar organics such as those classes of compounds expected to be ozonation disinfection by-products (low molecular weight aldehydes, ketones, acids, peroxides and epoxides).

This is not to say that methods for these classes of compounds do not exist. For example, a relatively recently published method to analyze low molecular weight aldehydes by aqueous derivatization followed by gas chromatography with electron capture detection

(GC/ECD; Glaze *et al.*, 1989a) has gained wide acceptance and has been used in several studies of drinking water disinfection by-products (Krasner *et al.*, 1989, Jacangelo *et al.*, 1989; Glaze *et al.*, 1989a; Sclimenti *et al.*, 1990). Also, texts such as that compiled by Knapp (1979) contain descriptions of a multitude of possible techniques which may be attempted. In general, however, existing methods for other disinfection by-products are either very complicated procedures or require instrumentation not typically found in water treatment plant laboratories.

Because of the polar nature of many ozonation byproducts, they are not amenable to the gas chromatographic techniques which have been applied to many chlorination byproducts. In their comprehensive review, Sheldon and Smith (1989) propose an analytical scheme for polar organics in drinking water, with particular application to disinfection byproducts. They place particular emphasis on high performance liquid chromatography (HPLC), and mention supercritical fluid chromatography (SFC) as an alternative technique. However in the present research, possible analytical techniques considered were limited to those involving gas chromatography as this was the instrumentation available.

The Analytical Chemistry journal editors biennially engage scientists to produce literature reviews encompassing a wide range of topics related to the analysis of chemicals. Smith and Patterson (1990) wrote a review related to the analysis of various functional groups including some expected to be produced on ozonation such as acids, alcohols, aldehydes and ketones, among others. From this review, gas chromatographic methods for carboxylic acids included pentafluorobenzyl bromide derivatization followed by GC/ECD (Thio *et al.*, 1988), although most methods cited utilized HPLC and none involved analysis at the low concentrations expected to be encountered in drinking water. Additional investigation of the literature provided details of several other methods for the analysis of carboxylic acids, among them an aqueous derivatization method utilizing GC/ECD described by Wong *et al.* (1988). These methods are summarized in Table 1.1.

No new GC methods were described for analysis of alcohols or amides in the review written by Smith and Patterson (1990). There are several sensitive and simple methods for amines analysis, including one involving aqueous derivatization with perfluoroacetyl chloride followed by GC/ECD (Coutts *et al.*, 1981, 1984). Amino acids can be similarly determined using pre-esterification with acidic isobutanol followed by derivatization with pentafluorobenzoyl chloride and GC/ECD analysis (Yeung *et al.*, 1986).

Phenols can be derivatized in non-aqueous solutions with pentafluorobenzoyl chloride then analyzed by GC/ECD (Coutts *et al.*, 1979, 1980; Winkeler and Levsen, 1989 in Smith and Patterson, 1990) or by direct aqueous acetylation followed by gas chromatography with flame ionization detection (GC/FID; Janda and Langenhove, 1989 in Smith and Patterson, 1990).

Aldehydes and ketones still seem to be best analyzed by pentafluorobenzyloxyamine derivatization with GC/ECD analysis (Glaze *et al.*, 1989a; Sclimenti *et al.*, 1990). The method is simple and sensitive (low µg/L) and has been used for the analysis of drinking water (for example, Krasner *et al.*, 1989). At the initiation of the present research, it had also been suggested that this method could be expanded to include oxoacid compounds such as pyruvic acid by using diazomethane derivatization following pentafluoro-benzyloxyamine derivatization (Yamada and Somiya, 1989). Efforts made during this research and by others (Xie and Reckhow, 1992) showed this to be true.

1.7 Summary and Identification of Research Needs

Ozonation of natural organic matter (NOM) can lead to the production of by-products which are either toxicologically or otherwise biologically significant. During drinking water disinfection, NOM reacts with ozone in both molecular form and as hydroxyl radicals to form oxygenated disinfection by-products (DBPs) having reduced colour and molecular weight. Aldehydes, ketones and carboxylic acids are all formed

Table 1.1 Analytical Methods for the Determination of Carboxylic Acids in Water

METHOD	ADVANTAGES	DISADVANTAGES	REFERENCES
DAI--GC/FID	simple with no sample prep except pH adjustment	insensitive (mg/L), not good for oxalic acid (T>140°C thermal decomposition)	Jan Duisterwinkel *et al.* 1986; Fussell & McCaulley 1987; Hordijk *et al.* 1990
Extract--GC/TCD	simple	insensitive (mg/L)	Allen *et al.* 1987
CH_2N_2--GC/FID	simple, rapid, no H^+/ req'd so limits possible sample decomposition	pre-ext. &/or drying req'd, hazardous reagent generation, sensitivity mg/L	*e.g.* Molnár-Perl *et al.* 1985
$NH_2OH.HCl$--CH_2N_2--GC/FID	includes oxo- and hydroxycarboxylic acids	aq. deriv C=O, ext., COOH deriv.	Liebich & Dotzauer 1989
H^+/ROH--GC/FID	ROH=IBA, (isobutanol/acetyl chloride)	possible sample decomp. from high deriv temp. and H+ (at least mg/L sens.)	MacKenzie & Tenaschuk 1979-86;
	ROH=n-butanol, AQUEOUS DERIV.	xs n-but and Na_2SO_4 req'd, maybe ok to mg/L	Molnar-Perl *et al.* 1984-85
	ROH=BF3-butanol	req. drying first, possible sample decomposition from high temp. req'd and H+ (180µg/L ox acid in 1mL or 50mL sample)	Kawamura *et al.* 1985
PFBBr--GC/ECD	sensitive (µg/L) and derivatizes OH-acids as well as acids (TCE for acids only)	requires CN-column clean-up to remove unreacted PFBBr	Daneshvar & Brooks 1988
	extractive alkylation simpler than above	reagent purification necessary, uses dual oven GC	Jacobsson *et al.* 1988
	XAD-2/PFBBr reduces reagent interferences, also derivs phenols & barbituric acids	Somewhat involved method	Rosenfeld *et al.* 1984 see also Sithole *et al.* 1986 re:reagent purity see also EPA Meth604
DCC/PFP--GC/ECD	sensitive, extractive alkylation	unknown matrix effects	Wong *et al.*, 1988
PFBOA--CH_2N_2--GC/ECD	sensitive (µg/L) and applies to aldehydes, ketones and oxoacids	sim to $NH_2OH.HCl$--CH_2N_2--GC/FID method but more sensitive	Yamada & Somiya 1989
DNPH--GC/ECD?/NPD?	aqueous deriv., usually for HPLC analysis	DNPH must be recrystallized before use	Kieber & Mopper 1990
IonExch--DBAP--GC/ECD	sensitive (lo µg/L)	very complicated and labor intensive	Barcelona *et al.* 1980
BSTFA--TMCS--GC/FID	<50 µg/L possible with 1 mL plasma (France *et al.* 1988)	requires extraction with EtOAc and drying prior to deriv.	Lopez *et al.* 1985; France *et al.* 1988
$NH_2OH.HCl$--BSTFA+TMCS--GC/FID	get keto- polycarboxy- hydroxy- aromatic acids and saturated and unsaturated acids	requires extraction with EtOAc and drying prior to deriv. and can lose short chain acids - therefore use with steam distillation	Daolio *et al.* 1989; Wurth *et al.* 1989; Lefevere *et al.* 1989

during ozonation of aquatic NOM. Toxicological data on these by-products are limited, but they show that some DBPs could be of health concern. Aldehydes, including for example formaldehyde, acetaldehyde glyoxal and methylglyoxal, are known or suspected mutagens and carcinogens. Carboxylic acids are not considered a direct toxicological hazard but may be a significant component of the substrate (termed assimilable or easily biodegradable organic carbon) for growth of microbes in the distribution system which can deteriorate the quality of distributed drinking water.

In addition, chlorine or chloramine used to maintain distribution system disinfection may react with NOM or ozonation DBPs to form halogenated DBPs (XDBPs) including trihalomethanes, haloacetic acids, chloral hydrate and cyanogen chloride. XDBPs are also of health concern and maximum contaminant levels (MCLs) have been proposed or are in place for them. Some researchers have studied XDBP formation using formation potential or simulated distribution system approaches to examine halogenation reactions in complete natural water matrices. Investigations using fractionated NOM have also been reported in which different fractionation schemes were used from that reported herein.

In order to study DBP formation from NOM oxidation under controlled conditions, NOM must first be isolated from natural sources. Adsorption to resins such as Amberlite® XAD-8 has become standard practice. Data are available detailing these procedures and describing the materials isolated. However, humic substances adsorbed to XAD-8 resin account for only approximately 50 % of the organic carbon content of the source water and while these materials account for most of the colour, they likely underestimate DBP formation. Methods to improve recovery of this material or to further fractionate it for various purposes, including DBP studies and evaluation of treatment options, continue to be developed.

In order to be as comprehensive as possible in evaluating DBP production on ozonation, analytical methods for some classes of expected DBPs would have to be developed or adapted from those used for applications other than drinking water analysis.

In particular, these would include methods to determine carboxylic acids and oxoacids, compounds which would be expected to contribute to distribution system instability, and which may be of toxicological interest.

CHAPTER 2

RESEARCH OBJECTIVES

This research examined the production of disinfection by-products (DBPs) of natural organic matter (NOM), both in actual aquatic matrices and as fractionated material, to determine the effects of various ozonation operational parameters on DBP formation and possible origins for some DBP classes. The major objectives of this research were to:

1. Develop analytical methods for aqueous polar organic compounds as needed.
2. Identify ozonation DBPs formed under typical water treatment conditions, particularly those classes of which may be expected to be of potential health risk, either from direct contact with human life or by enhancing unsafe microbial conditions in drinking water.
3. Determine the effects of ozone on the formation of chlorination and chloramination DBPs.

Analytical methods were lacking for aqueous polar organic compounds such as those expected to be by-products of ozonation (low to mid molecular weight aldehydes, ketones, acids, enals). Their development as part of this research allows a more comprehensive evaluation of alternative processes such as ozonation which could become more important for the treatment of Canadian drinking water as research reveals shortcomings of processes currently in use.

As ozonation is currently the alternative drinking water treatment method showing the most promise, two additional objectives of this study were to use the methods developed above to identify ozonation by-products formed during typical surface treatment and to identify those of potential health risk. Considerable effort was expended on characterization of organic material in the raw water to enable causal relationships between raw water quality and the formation of different classes of by-products to be studied.

Examination of post-ozone chlorination and chloramination by-products was also included in this research. Since ozone produces assimilable organic carbon from natural organic matter and does not leave an oxidant residual following application, it cannot be used as the final disinfectant in a drinking water treatment plant. Current practise is that another disinfectant, typically chlorine or chloramines, is applied to maintain a disinfectant residual in the distribution system. In the case of post-chloramination, this provides a lasting disinfectant residual without the formation of unacceptable levels of chlorination by-products such as trihalomethanes (THMs), some of which are known carcinogens. The THMs as a class are currently regulated to 350 μg/L for drinking water, with new limits as low as 50 μg/L being considered. The practise of post-chloramination would likely be continued even if ozone were to be widely accepted as a primary disinfectant. Since ozone is being considered as an alternative to chlorine and chloramination is directly related to chlorination, it was considered prudent to determine the effects of post-chlorination and post-chloramination on ozone-disinfected water, especially for formation of by-products such as THMs.

In summary, this research was intended to improve current analytical procedures or adopt new ones to increase recovery and identification of ozonation by-products, and to study the effects of ozonation on the formation of post-chlorination and post-chloramination by-products of health concern. The identification of by-products in this research will facilitate the subsequent assessment of their toxicological significance.

CHAPTER 3

MATERIALS AND METHODS

This chapter presents details of methods used in all aspects of the research performed for this thesis. Additional information regarding methods development procedures and results may be found in Appendix I.

3.1 Reagents and Glassware

Water for the preparation of all solutions was distilled and then treated with a small scale treatment system (Milli-Q®, Millipore Corp.) composed of granular activated carbon and ion exchange cartridges. Water used in ozonation experiments was first treated with the Milli-Q® system, then made ozone-demand-free by bubbling 40 mg/L gaseous ozone in oxygen at 50 mL/min for 15 minutes, then storing it overnight to let the ozone residual dissipate. The fulvic acid solutions prepared with ozone-demand-free water were buffered to specified pH values using phosphate buffers prepared in house unless otherwise stated.

Disinfection by-product standards and laboratory reagents (acids, bases, phosphates for buffers, derivatization reagents) were obtained at greater than 98 % purity and were used as received unless otherwise stated. Indigo trisulfonate was obtained and prepared for ozone residual determinations as described in Standard Methods (APHA-AWWA-WEF, 1992). Diazomethane was generated in mmol amounts from 1-methyl-3-nitro-1-nitrosoguanidine (MNNG, Aldrich) and sodium hydroxide, and was stored in diethyl ether solution at ≤ 0°C until use (maximum storage time 7 days). Amberlite® XAD-8, XAD-4 and Bio Rad® AG MP-50 resins used to isolate the aquatic NOM were Soxhlet cleaned by the procedures described by Malcolm (1991). Humic and fulvic acid standards, which had been isolated from the Suwannee River in the United States, were purchased from the International Humic Substances Society (IHSS, 1990) and were used as received.

Sodium sulfate crystal (Fisher Scientific Ltd.) was baked at 450 to 550 °C for at least 4 hours before use.

All glassware used was of the highest grade available and was cleaned at 85 °C in a stainless steel dishwasher (Miele) employing 2 acid washes with phosphoric acid and two distilled water rinses. Glassware used in ozonation experiments was made ozone-demand-free by rinsing with Milli-Q® water having a measurable ozone residual prior to use. That used in chlorination and chloramination experiments was made chlorine-demand-free by adding Milli-Q® water and reagent grade sodium hypochlorite (Fisher Scientific Ltd.) to a concentration of approximately 10 mg/L as Cl_2 and allowing it to react at least 4 hours, usually overnight, prior to use. Caps and stoppers for all pieces of glassware were either made of glass or were lined with Teflon®.

3.2 Isolation and Characterization of Aquatic Natural Organic Matter

3.2.1 Sampling

In this research, NOM was isolated on XAD-8 resin followed by XAD-4, and later also AG-MP 50 resin, from two surface water sources. One source (Driedmeat Lake) was a surface water of relatively high non-volatile dissolved organic carbon (NVDOC) content (10 to 20 mg C/L). This Lake supplies the City of Camrose, Alberta with source water for its drinking water treatment plant. The lake is shallow, having an average depth of 2.2 m, and experiences problems in the summer months with algal blooms. It was sampled during mid- to late September following completion of XAD resin preparation and while DOC levels remained high. Samples were obtained from a point prior to the pre-chlorination stage of the treatment plant to avoid contamination with chlorinated material not normally present in the raw water. The second site was the North Saskatchewan River at the main supply line to the E.L. Smith Water Treatment Plant in Edmonton, Alberta. This supply provided raw surface water of relatively low organics concentration (typically 2 to 3 mg/L NVDOC). Consideration was given to using the supply line for the Rossdale water treatment pilot plant, previously used for studies funded by Health and Welfare Canada, but the E.L. Smith site was chosen because of its location upstream of urban inputs to the river.

Driedmeat Lake was sampled once on September 26, 1991 using 15 glass carbuoys of nominal 14, 19 or 23 L capacity resulting in an approximate total sample volume of 300 L. The North Saskatchewan River water was sampled twelve times between December 13, 1991 and February 21, 1992 for an approximate total sample volume of 2100 L. Sincere appreciation is extended to all those who helped in the transport of these heavy carbuoys.

Upon return to the laboratory, samples were immediately acidified to pH 2.0 ± 0.1 (Fisher Accumet® pH meter Model 610A, Fisher Scientific, USA) with approximately 7 to 12 mL concentrated sulfuric acid (maximum 1 hr delay). Following acidification, filtration was initiated immediately; however, suspended solids would quickly clog the filters so only an amount necessary to continue adsorption efforts was filtered immediately. The remaining carbuoys were stored at least overnight at 4°C in the dark prior to filtration and resin adsorption to allow time for some particulates to settle prior to filtration, improving filtration speed and extending membrane filter life.

3.2.2 Filtration

The apparatus employed to filter the large volumes of sample required is shown in Figure 3.1. Sample was vacuum filtered (25 psi vacuum, Millipore® vacuum pump) through a 1.5 µm pore size Whatman 934-HA (Fisher Scientific) glass prefilter followed by a 0.45 µm pore size Durapore® (Waters) membrane filter housed in a stainless steel pressure filtration unit which was completely lined with Teflon® (Sartorius®; on loan from the Department of Medical Microbiology). Filters were 90 mm in diameter, and all pieces of water-contacting tubing and connectors were made of glass, stainless steel or Teflon®.

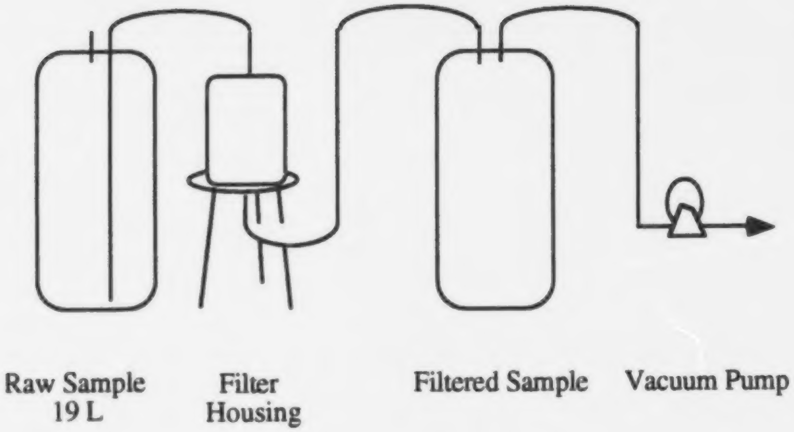


Figure 3.1 Apparatus Used to Filter Raw Water Samples Prior to NOM Isolation

The prefilters were particularly useful for the filtration of lakewater, which had a high suspended solids content, and they often extended the life of the 0.45 μm filters from less than 1 L sample to greater than 10 L. However, they generally had little effect on the filtration of river water. In many cases, most of the particulates would pass through the prefilter and be caught on the 0.45 μm filter, plugging it before a 10 L throughput was achieved.

The filtration step was the most time-consuming part of the NOM isolation procedure. Fortunately, some help was obtained in performing some of the filtration duties from Mr. S.L. Zhang, a Ph.D. student with Dr. Huck who preferred to work later shifts, in exchange for some future collaborative work using the NOM obtained.

Following filtration, the pH of the samples was rechecked and, if necessary, readjusted to pH 2.0 ± 0.1 with concentrated sulfuric acid. They were then either stored at 4°C until further processing or immediately subjected to the resin adsorption procedure.

3.2.3 XAD Resin Adsorption (Humic and Fulvic Acid Isolation)

Humic and fulvic acids in the filtered sample were adsorbed to Amberlite® XAD-8 and XAD-4 resins in series using the apparatus shown in Figure 3.2. The configuration shown was the final in a series of variations which eventually provided the greatest degree of unattended operation. Two of these adsorption trains were used simultaneously. The columns of cation exchange resin were added to the end of each XAD resin adsorption train partway through the isolation of NOM from river water and were not in use during lakewater NOM isolation. Their operation is discussed in Section 3.2.8.

The XAD-4 and XAD-8 resins were held in cartridges made of stainless steel and Teflon®, construction details of which are specified elsewhere (Huck, 1986). Each cartridge held 300 mL resin.

In total, 2100 L river water and 300 L lakewater sample were passed through the apparatus. Filtered sample at pH 2.0 ± 0.1 was pumped through each of the two

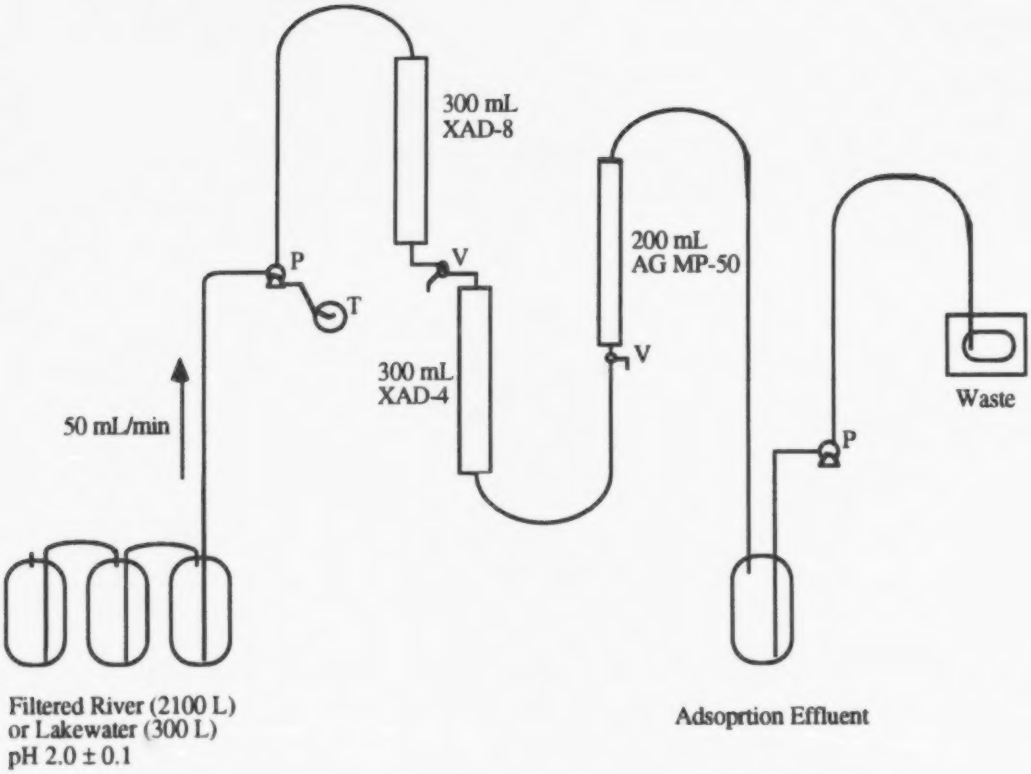


Figure 3.2 Apparatus for Isolation and Fractionation of Natural Organic Matter (P = Masterflex® peristaltic pump; T = timer; V = glass or stainless steel three way sampling valve)

adsorption trains at a nominal flow rate of 50 mL/min, corresponding to approximately 10 bed volumes per hour as recommended by Malcolm (1991). The pumps used were Cole-Parmer Masterflex® peristaltic pumps. All connecting tubing was 1/4 inch or 3/8 inch internal diameter Teflon® except for a 12 inch section of 1/8 inch internal diameter Viton® tubing located in the pump heads. All connecting unions and fittings were made of stainless steel. A two way valve placed between the XAD-8 and XAD-4 resin cartridges facilitated humics breakthrough monitoring for each resin. One train utilized a stainless steel two way valve while the other train used a valve of glass and Teflon® (due to availability).

NOM was adsorbed from filtered water samples in batches of approximately 200 L, and each sample batch was monitored at least three times during its adsorption. The resin in the XAD cartridges would then be desorbed as described in the next section, and after approximately 600 L of water had been treated it was replaced with freshly cleaned resin.

Monitoring of the adsorption procedure was necessary to assess resin adsorption performance under long term use conditions, to aid in the estimation of product yield, and because the stainless steel resin cartridges did not permit visual monitoring of the advancement of the adsorption front. Samples were obtained following each of the resin cartridges or columns and from the sample carbuoys. NOM breakthrough was monitored by measuring non-volatile dissolved organic carbon (NVDOC; DC 80 Total Carbon Analyzer, Xertex Dohrmann) and UV absorbance at 254 nm (Spectronic 601, Milton Roy Co.). Colour (measured at 420 nm following addition of 5 M sodium hydroxide to pH 11) was not used as a routine monitoring parameter for both sources because of the extremely low concentrations of coloured material in river water, and because the lakewater adsorption monitoring results showed that the UV and colour data were consistently very similar (see Appendix II). Therefore, measurement of both parameters on a routine basis was deemed unnecessary. Results of adsorption monitoring efforts are presented in

Chapter 4 and in Appendix II. The relative values of UV absorbance and NVDOC as monitoring parameters are discussed therein.

3.2.4 XAD Resin Elution

Each of the XAD-4 and XAD-8 resin cartridges was individually eluted with 0.1 M sodium hydroxide in the reverse direction to adsorption as described by Malcolm (1991) but with minor modifications. The most notable deviation was that non-'center cut' fractions were not collected separately but rather the total elution volume was collected and reconcentrated on smaller (200 mL) resin columns prior to humics and fulvic acids separation.

The resins were desorbed by drawing 0.1 M sodium hydroxide through the cartridges in the reverse direction to adsorption at approximately half the flow rate as for adsorption (nominally 25 mL/min) to provide a more concentrated eluate. The same peristaltic pumps used for adsorption were placed following the resin cartridges, and controlled by a single rheostat which reduced the flow in each train equally. Eluate was collected and stored in pre-cleaned 3 L sulfuric acid bottles with Teflon®-lined caps. Elution progression was monitored visually. During elution of the 'center cut' the colour of the eluate as it passed through the Teflon® connecting tubing was a dark purple due to refraction through the Teflon®. The XAD-8 resin consistently produced a much more highly coloured eluate than did the XAD-4 resin.

All portions of eluate were reconcentrated prior to humic and fulvic acids separation in a similar manner to that reported by Malcolm (1991). Glass columns containing 200 mL XAD-8 or XAD-4 resin were used for this purpose. Desorption of the reconcentrated humics was performed at a flow rate of 25 mL/min to reduce the total volume of desorbate. Once the 'center cut' appeared to have been mostly eluted, the flow rate was increased to approximately 50 mL/min until most of the remaining colour appeared to be eluted. At that time, the eluant was switched from 0.1 M sodium hydroxide to 0.1 M sulfuric acid until the eluate was acidic to pH paper to prepare for the next adsorption run.

3.2.5 Separation of Humic and Fulvic Acids

The humic acids from each of the XAD-8 and XAD-4 combined reconcentrated eluates were isolated from the fulvic acids according to the procedure outlined by Malcolm (1991). Each combined NOM isolate was acidified to pH 1.0 ± 0.1 using concentrated sulfuric acid and cooled to 2°C in a refrigerator. When removed from the refrigerator, the isolates were placed on ice. Precipitated humic material was resuspended many times over at least a 24 hour period before being centrifuged to separate the precipitated humics from the dissolved fulvics.

The XAD-8 concentrates of river and lakewater NOM were the only ones to develop significant precipitate. Little or no precipitate (<10 mg estimated) was detectable in corresponding XAD-4 concentrates.

After cooling and repeatedly resuspending the concentrates at 2°C they were centrifuged using an International Clinical Centrifuge Model CL (International Equipment Co., Needham Hts., Mass.) and 50 mL centrifuge tubes borrowed from another research group within the Environmental division. Four tubes were used for this purpose.

Balanced sample portions were centrifuged at 3030 rpm (± 1%) for 10 minutes at somewhat less than room temperature. This unit is not thermostatted, so ice was added to the centrifuge prior to starting it as a coolant to prevent the solutions from being warmed to near or above room temperature because of air friction within the unit. As well, the centrifuge tube holders were placed in the freezer for 5 to 10 minutes before each use to aid in maintaining sample refrigeration. All sample portions and centrifuge tubes were kept on ice as much as possible.

Following separation, the precipitated and centrifuged XAD-8-derived humic material was subsequently stored at 2°C in two of the 50 mL centrifuge tubes, and the solution of XAD-8-derived fulvic material was retained in a 1L Wheaton bottle at 2°C. The resulting XAD-8-derived fulvic acid solution was not cloudy, even after standing overnight at 2°C, indicating that the cooling procedure employed during centrifugation was adequate for preventing the redissolution of precipitated humic material.

3.2.6 Desalting, Hydrogen-Saturation and Freeze-Drying

Elimination of salts from the isolated humic and fulvic acids was accomplished in general by methods described by Malcolm (1991). Glass columns of 200 mL capacity each having a porous glass frit (type B, 70-100 µm pore size) were loaded with 175 mL of XAD-8 or XAD-4 resin (to desalt isolates from these resins) or 150 mL of 100-200 mesh Bio-Rad AG®50W-X8 cation exchange resin (to hydrogen-saturate all desalted isolates). Methanol used to store the pre-cleaned resins was removed with 100-200 column volumes of Milli-Q water. The XAD resins were pre-eluted with 200 mL 0.1 M NaOH to remove Milli-Q water impurities adsorbed during the initial wash and then re-acidified with 0.1 M sulfuric acid prior to loading the isolated humic or fulvic acids.

The humic and fulvic acid solutions were basified with 0.1M NaOH until all precipitate dissolved. Then they were pumped from the bottles in which they were stored to the top of their respective XAD resin columns and loaded onto the resin at a flow rate of 20 mL/min. Once enough fulvics had been loaded to colour the top third of the resin bed, the column was eluted with Milli-Q water (5 mL/min). The effluent was monitored for conductivity (YSI Model 33 S-C-T conductivity meter, Yellow Springs Instrument Co. Inc., Yellow Springs ,Ohio) until it was less than 250 µmho.

The desalted humic acids were eluted from the XAD resins in the reverse direction to adsorption with 0.1 M sodium hydroxide at 10 to 20 mL/min flowrate. Eluate was then pumped either directly from the top of the XAD column or from a receiving vessel to the top of the cation exchange resin column for removal of sodium (hydrogen saturation). The flowrate during hydrogen saturation was 10 to 20 mL/min. If the flow was any higher than that, the ground glass connectors would pop off. As sodium and hydrogen ions were exchanged, the resin colour changed from orange to brown, which allowed its loading to be judged visually. Several solutions could be hydrogen saturated before the resin required regeneration. Final pH of the hydrogen saturated solutions was between pH 3 and pH 4.5.

Volume reduction of the hydrogen-saturated isolates prior to final freeze-drying was attempted using rotary evaporation (Buchi Rotavapor-R, Brinkmann, Rexdale, Ont.) at room temperature as recommended by Malcolm (1991). This step was not successful and so was eliminated from the sample preparative protocol.

Samples were freeze-dried using a Labconco® Freeze Drier 4.5 (Labconco Corp., Kansas City MO). The 500 to 1000 mL final isolate solutions were each split into two to three portions for freeze-drying. Once dried, as much of the material possible was transferred from the freeze-drying flasks to preweighed 40 mL sample vials and stored refrigerated until further use. However, a significant amount of the dried material was difficult to recover from the freeze-drying flasks, either because it stuck to flask walls or because of a build-up of static electricity. Therefore, the dried material remaining in the flasks was redissolved in reagent water, transferred to smaller flasks (100 mL) and re-freeze-dried. Newly dried material was recombined with corresponding material in the 40 mL vials and stored in the refrigerator. The overall freeze-drying procedure, including residue recovery, required approximately 4 days time per run.

3.2.7 Resin Cleaning and Isolation of Hydrophobic Neutral Components

On completion of the NOM isolation procedure, the XAD-8 and XAD-4 resins were removed from the sampling cartridges and cleaned by Soxhlet extraction (as recommended by Malcolm (1991) for initial resin cleaning) to yield another fraction of river water NVDOC termed the hydrophobic neutral components (Leenheer, 1981). Although adsorbed humics had been desorbed with sodium hydroxide, the resins in each cartridge retained a yellow-to-orange colour. This may have been due to a partial aggregation of humic matter at the low pH used for adsorption, and its subsequent entrapment within the resin pores (Town and Powell, 1993). The resin at the cartridge influent end retained most of the colour while that at the cartridge effluent was nearly colourless, with the colour gradient between both ends similar to that described in Section 4.1 for the adsorption trial runs (most of the colour being in the top third of the resin column). Since the resins were to be cleaned anyway, recovery of this material did not require much additional laboratory time.

During resin cleaning with methanol, most of the colour was removed from both resin types in the first 2 to 3 Soxhlet cycles. These methanol fractions were combined and rotary evaporated to final volumes each of approximately 50 mL. The hydrophobic neutrals did not remain in solution during rotovapping but formed an orange oil or grease which grew darker as the evaporation progressed (4 to 6 hr). The final XAD-8- and XAD-4-derived extract solutions were actually aqueous rather than methanolic because the resins were not dried prior to Soxhlet extraction and the rotovapping simply removed the methanol. These solutions were freeze-dried overnight. Final hydrophobic neutral isolates were either black semisolids or oils. These freeze-dried isolates were redissolved in approximately 7 mL methanol and were evaporated under a gentle stream of nitrogen to a near constant weight to estimate yields (Table 4.2). Unfortunately, however, testing of this material was not within the scope of the present research, therefore it was stored at 4 °C under nitrogen for possible future experimentation.

3.2.8 Cation Exchange Resin Isolation of Hydrophilic Bases

In an effort to recover a larger portion of the aquatic NOM, filtered samples were passed over cation exchange resin following XAD-8 and XAD-4 adsorption (Figure 3.2). The resin was not available during NOM isolation from lakewater and so was only applied to river water NOM isolation. This was also an attempt to increase the recovery of nitrogen-containing compounds as many amino-compounds are cations at ambient pH and below. Other researchers have used cation exchange resins as part of their humics isolation protocol (for example, Leenheer and Noyes in Hayes *et al.*, 1989a and Leenheer, 1981).

Bio Rad® AG MP-50 resin, a strongly acidic cation exchanger with bonded sulfonic acid active groups, was used for the procedure. The relative affinities of AG MP-50 resin for cations are listed in Table 3.1. Enough resin for 2 x 150 mL columns was prepared by first Soxhlet cleaning as for the XAD resins. Following cleaning, 150 mL resin was loaded into each of two glass columns of approximately 250 mL capacity, and impurities were desorbed with 2 M sodium hydroxide and hydrogen saturated with 3M hydrochloric acid.

Calculations of resin capacity for hydrophobic bases were made as described by Leenheer (1981). Using the sample conductivity, the sample ionic concentration was estimated from:

$$\text{meq salt/L} = 12.5 \times (\text{specific conductance in mmho, } 25^\circ\text{C}) \qquad (3\text{-}1)$$

Since the resin has a lower affinity for sodium ion than for ammonium ion or, presumably, ionized organic amines, and hydrogen ion in acidified samples displaces sodium ion before ammonium ion, Leenheer had determined that the sample volume adsorbable prior to ammonium ion breakthrough could be calculated from:

$$V_e = (686 \times \text{grams resin}) + V_o \qquad (3\text{-}2)$$

assuming a relatively low sample salt concentration (less than 572 μmho specific conductance), pH 2 and 25 °C. Using $V_o = 75$ mL, the resin breakthrough volume for 250 μmho water was calculated to be (686 mL/g x 120 g) + 75 mL = 82.4 L. To be safe, and as recommended by Leenheer (1981), 41 L rather than 82 L was used as the estimated maximum sample volume adsorbable before breakthrough.

Table 3.1 Relative Affinities of Bio Rad AG MP-50 Resin for Cations*

Resin Counterion	Relative Selectivity
H^+	1.0
Li^+	0.85
Na^+	1.5
NH_4^+	1.95
Mn^{2+}	2.35
K^+	2.5

* Bio Rad Catalogue

The ion exchange columns were operated in upflow mode (23 % bed expansion at 50 mL/min flow rate) for several reasons. First, the flow rates employed during adsorption caused enough back pressure to build in downflow operation to blow the ground glass connectors. Sample collection for monitoring purposes was more difficult in downflow mode. Also, when more unattended operation became possible with the system, specifically when the system could be shut down by means of timers when the filtered water supply was estimated to be low, small leaks in ground glass connections caused the ion exchange columns to run dry if they had been operated in downflow mode, which is undesirable. The effect of upflow as opposed to downflow operation of these columns on the overall recovery of the hydrophilic bases component of the NVDOC was determined experimentally to be minimal and is further discussed later in this section.

Breakthrough monitoring for the ion exchange resins was initially via conductivity and NVDOC measurements, however these both proved to be ineffective monitoring parameters. The conductivity of raw sample was on the order of a few hundred μmho whereas that of the acidified sample was typically greater than 2200 μmho. Small changes in conductivity were difficult to detect, and without a flow cell the task was even more difficult. NVDOC monitoring proved to be impractical given the time required to collect and analyze samples versus sample throughput rate. Therefore, initially, the ion exchange resins were arbitrarily desorbed following every 40 to 50 L sample adsorbed per column (80 to 100L total sample throughput) and it was hoped that the Leenheer breakthrough estimates were correct.

Later, the concentration of hydrophilic bases on ion exchange resin was monitored by flame photometry (Evans Electroselenium Ltd., Halstead, Essex, England). Sodium ion is eluted from the ion exchange columns by acid present in the sample before amino-compounds, and potassium ion elutes at approximately an equal volume following amines elution (considering their relative resin selectivities). The results of a test done to assess Leenheer's resin capacity estimates and determine the effect of upflow versus downflow operation are shown in Figure 3.3. Samples of XAD-4 effluent and ion exchange effluent were obtained at several times over an 8 hour period and analyzed for sodium and potassium ions (Na^+ and K^+) relative to filtered water (XAD-8 influent) which was used to set the instrument to full scale. The results for K^+ are not shown in Figure 3.3; K^+ was always completely adsorbed to the ion exchange resin throughout the course of the experiment. The blank was Milli-Q® water.

Breakthrough curves for Na^+ for the upflow and downflow operated columns are classically shaped and are nearly identical, especially for sample volumes less than 30 L which represents approximately 50 % breakthrough. This indicated that upflow operation at the flow rates employed was not detrimental to the efficiency of the procedure. Also, as expected, neither of the XAD-8 nor XAD-4 resins, nor substances adsorbed to them, removed Na^+ or K^+ ions from solution.

As for column capacity for ions in NSR water, considering that no K^+ breakthrough was detected even for 50 L throughput, the curves indicate that a 40 L capacity under the conditions tested is not unreasonable. Therefore, for ion exchange operation monitoring, the resin desorption schedule was determined by V_E calculations resulting from conductivity measurements on each batch of NSR water and checked by monitoring Na^+.

Resins were eluted by forward passage of 1 M ammonium hydroxide at a flow rate of approximately 10 mL/minute. They were re-hydrogen-saturated with 2 M hydrochloric acid and rinsed with several column volumes of Milli-Q® water prior to reuse.

3.2.9 NOM Fraction Characterization Methods

Selected NOM fractions were characterized by the following physical, chemical or spectroscopic methods for comparison with data available for the humic and fulvic acid materials obtained from the International Humic Substances Society, and for use in interpreting the results of subsequent ozonation experiments.

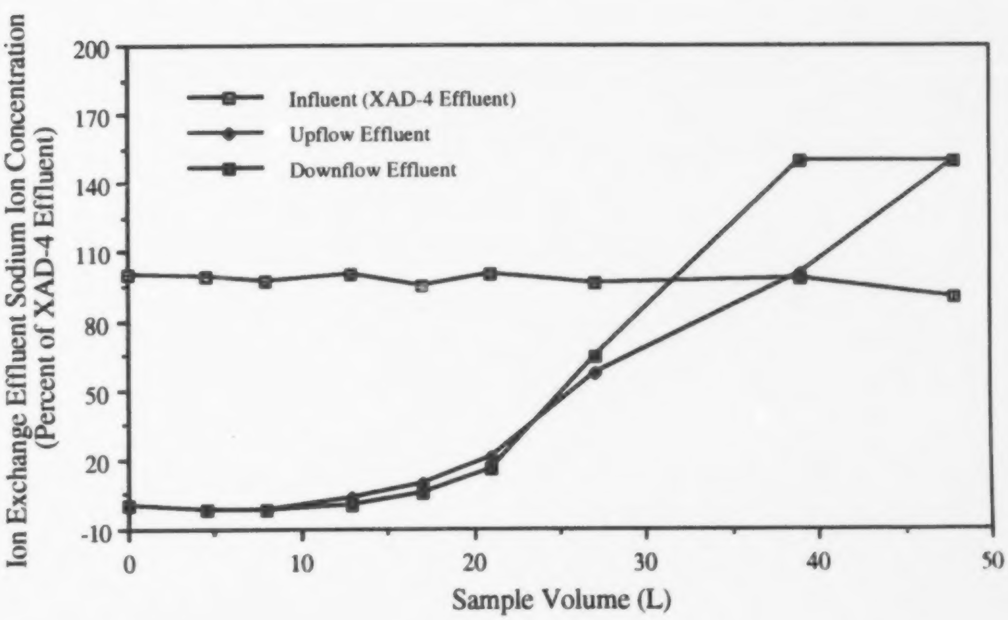


Figure 3.3 Effluent Concentrations of Sodium Ion Measured During Upflow and Downflow Ion Exchange Experiments

Immediately prior to freeze-drying, aqueous solutions of isolates were analyzed by UV/VIS spectrophotometry. Spectra of each solution were obtained from 190 to 800 nm using a Hewlett Packard scanning UV/VIS spectrophotometer. Samples were diluted, if necessary, to obtain representative spectra. Also, spectra were obtained for both acidic (pH 3) and alkaline conditions (pH 11) since solution colour was visibly different at the extremes of pH. A freshly prepared NaOH solution was used for pH adjustment of the acidic hydrogen-saturated isolates.

UV absorbance determinations were made at 254 and 270 nm (Spectronic 601, Milton Roy Co.) for comparison to values reported in the literature.

All other characterization analyses were performed by others as is described following. Staff at the University of Alberta Spectral Services laboratory analyzed the NOM fractions elemental content. Elements which were routinely determined were carbon, hydrogen, nitrogen, oxygen and sulfur. They were also responsible for obtaining Fourier-transform infrared (FT-IR; Nicolet) spectra (obtained from cast films) which are included in Appendix III.

Average molecular weights were determined by vapour pressure osmometry (Hayes *et al.*, 1982) at the Alberta Research Council in Devon, Alberta.

Attempts to characterize the NOM fractions by ^{13}C nuclear magnetic resonance (NMR) spectroscopy were made but were less successful than was hoped and were discontinued because of their expense. ^{13}C NMR data obtained from the Nuclear Magnetic Resonance Laboratory of the University of Alberta are contained in Appendix III.

3.3 Ozonation Procedures

Methods employed to perform the ozonation experiments are discussed herein. Included are a description of the factorial design of the experiments, specific details for ozonation experiments performed at high and low organics concentrations, and procedures employed for setting up subsequent formation potential tests. Details regarding analytical methods for the disinfection by-products studied are given in Section 3.4.

3.3.1 Factorial Design

For all fulvic acid fractions isolated on XAD-8 or XAD-4 resin, full 2^3 factorial experiments with three midpoints were conducted to investigate the effects of pH (6, 8), alkalinity (0, 200 mg/L as $CaCO_3$) and ozone dosage (1:1 and 3:1 applied ozone:NVDOC mass ratio) on DBP production and UV absorbance reduction as shown in Table 3.2. For those unfamiliar with factorial experimental design, a brief explanation can be found in Appendix IV. The values of these experimental parameters were chosen to encompass or exceed the range employed in current drinking water treatment practice and in consideration of estimated water quality parameters. The relatively high ozone dosages were employed to facilitate observation of resulting effects. The midpoint pH was chosen to be pH 6.3, representing the average hydrogen ion concentration between pH 6 and pH 8, and is a valid choice. The pH midpoint could also have been the average hydroxide ion concentration (corresponding to pH 7.7) and, in retrospect, considering the predominance of hydroxide ion in the mechanisms of ozone decomposition, base catalysis of chlorination reactions and hydrolysis of DBPs, this might have been the better choice.

Temperature was not included as a variable, and all experiments were performed at room temperature (nominally 20 °C). Also, the hydrophilic base fraction isolated by ion exchange was only investigated for pH effects due to limited quantities of available material.

The main effects and interactions for each variable were calculated for each of the DBPs according to Box *et al.* (1978). Also, mean responses for DBP yields ($\bar{y}$) were determined for each variable at both the high and low parameter levels, and the individual DBPs were arranged into classes and summed to provide a measure of compound class related effects. The compound class yields obtained at the two parameter levels were

Table 3.2 Parameters and their Values Employed in the Factorial Design Experiments

Parameter	Level		
	-	0 (Midpoint)	+
pH	6	6.3*	8
Alkalinity (mg/L as $CaCO_3$)	0	100	200
Ozone Dose (mg:mg ozone:NVDOC)	1:1	2:1	3:1

* pH 6.3 is the midpoint hydrogen ion concentration between pH 6 and pH 8.

compared using the t-test to determine if differences observed were significant. The confidence interval (CI) for these comparisons was calculated from:

$$CI = \text{mean effect} \pm (t_{df,\alpha/2})(\text{Var } \bar{y})^{0.5} \tag{3-3}$$

where $t_{df,\alpha/2}$ is the 't' statistic for the appropriate number of degrees of freedom at a level of significance of $100(1-\alpha)\%$, Var $\bar{y}$ is the variance in the values determined for the midpoints and n is the number of replicates. Var $\bar{y}$ is calculated from (Var y)/n. For these factorial experiments, the number of degrees of freedom was 6, the mean effects were compared at the 90 or 95 % level of confidence and the values of 't' corresponding to these criteria were 1.44 and 2.43, respectively. The resulting CI's have been tabulated in Appendices IV, VI and VII.

The individual CI's have not been stated throughout the text to avoid unnecessarily complicating it by reporting CI's for each comparison. After performing several of these calculations, it became apparent that if the difference between the DBP yields at the higher and lower parameter levels was greater than approximately 10% of the larger of the two values, then the difference could be considered significant at the 90% level of confidence. Because there are so many comparisons to be made in this research, the reader may use an approximate 10% difference criterion as a guide in identifying significant effects.

3.3.2 Ozonation of 20 mg/L NVDOC Fulvic Acid Solutions

A sample volume of 125 mL was employed for the ozonation experiments performed at 20 mg/L NVDOC, and ozone-demand-free (ODF) water was used throughout. The concentration of 20 mg/L NVDOC was chosen to enhance detection of DBPs, since prior studies had shown that ozonation of river water at approximately 1.5 mg/L NVDOC produced DBPs at or near analytical detection limits. Concentrated solutions of fulvic acid were prepared in ODF water, diluted to 20 mg/L as NVDOC for the experiments and analyzed to confirm their NVDOC concentrations (Xertex Dohrmann

DC80 Total Carbon Analyzer). Only fulvic acid fractions were used for these experiments due to the limited quantities available of other fractions, for example the humic acids.

Prior to ozonation, appropriate volumes of pH 6 or 8 buffer were added to 125 mL sample to a final phosphate concentration of 0.05 M. Phosphate buffers were used because they do not make a net contribution to the scavenging or promotion of radical species involved in aqueous ozonation reactions (Staehelin and Hoigné, 1985; see also Appendix I). Alkalinity was provided as required by adding sodium bicarbonate stock solution to result in 200 mg/L alkalinity as $CaCO_3$. Samples representing midpoints in the factorial design were adjusted to pH 6.3 (midpoint of hydrogen ion concentration) and 100 mg/L alkalinity prior to ozonation. pH measurements made during the tests confirmed that the target pH values were reached to within ± 0.05 units.

Gaseous ozone at 20 to 45 mg/L was generated from oxygen using a PCI ozone generator (Model C2P-9C-4; PCI Corporation, Stamford Conn.) and applied to the test solutions at a flowrate of 100 ± 1 mL/min. This method of ozonation was called semi-batch mode and was used for all ozonation experiments. This experimental nomenclature is consistent with that of other researchers in North America (Glaze *et al.*, 1992) who describe the procedure of adding pre-made ozone solutions to test solutions as being batch tests. Actual concentrations of ozone were determined prior to each experiment by potassium iodide reaction and amperometric titration with sodium thiosulfate (Standard Methods, APHA-AWWA-WEF, 1992). Ozonation times were adjusted to achieve either a 1:1 or 3:1 ratio of ozone to measured NVDOC (30 to 90 seconds for experiments at 20 mgC/L NVDOC).

Following ozonation, samples were immediately taken for ozone residual determinations (potassium indigo trisulfonate, Standard Methods, APHA-AWWA-WEF, 1992). Samples for disinfection by-products analyses (aldehydes, oxoacids and carboxylic acids; methods described in Section 3.4) were taken within 2 minutes of stopping ozonation. UV absorbance measurements were made at 254 and 270 nm approximately

2.5 to 3.5 minutes following the test. Another 40 mL of ozonated sample was retained and stored at 4 °C for possible future analysis.

3.3.3 Ozonation of 5 mg/L NVDOC Fulvic Acid Solutions

A sample volume of 500 mL was employed for the ozonation experiments performed at 5 mg/L NVDOC, and ozone-demand-free (ODF) water was used throughout. Concentrated solutions of fulvic acid were prepared in ODF water, diluted to 5 mg/L as NVDOC for the experiments and analyzed to confirm their NVDOC concentrations (Xertex Dohrmann DC80 Total Carbon Analyzer). All other details for these experiments were as described in Section 3.3.2, except for the following.

Gaseous ozone at 10 to 15 mg/L was bubbled into the test solutions in semi-batch mode at a flowrate of 50 ±1 mL/min to achieve a 1:1 or 3:1 ratio of ozone to measured NVDOC (corresponding to 1 or 3 minutes ozonation time). A 10 minute post-ozonation time was employed in the experiments at 5 mgC/L prior to sampling for ozonation DBPs, ozone residual or UV absorbance. This allowed slower reactions to progress more nearly to completion before sampling, and approximated actual water treatment practice. When the UV absorbance of selected ozonated samples was followed over a 20 minute period (shown in Figure 3.4), it was apparent that the ozonation reactions (at least those involving UV absorbing species) were complete within the 10 minute waiting period, and that reactions appeared to be complete in as little as 3 minutes.

Following the 10 minute post-ozonation reaction time, samples were taken for ozone residual determinations (potassium indigo trisulfonate, Standard Methods, APHA-AWWA-WEF, 1992), disinfection by-products analyses (aldehydes, oxoacids and carboxylic acids; methods described in Section 3.4), and UV absorbance measurements (254 and 270 nm). Another 40 mL of ozonated sample was retained and stored at 4 °C for possible future analysis. Two aliquots of 150 mL sample were also taken for determination of the formation potentials for several halogenated disinfection by-products resulting from

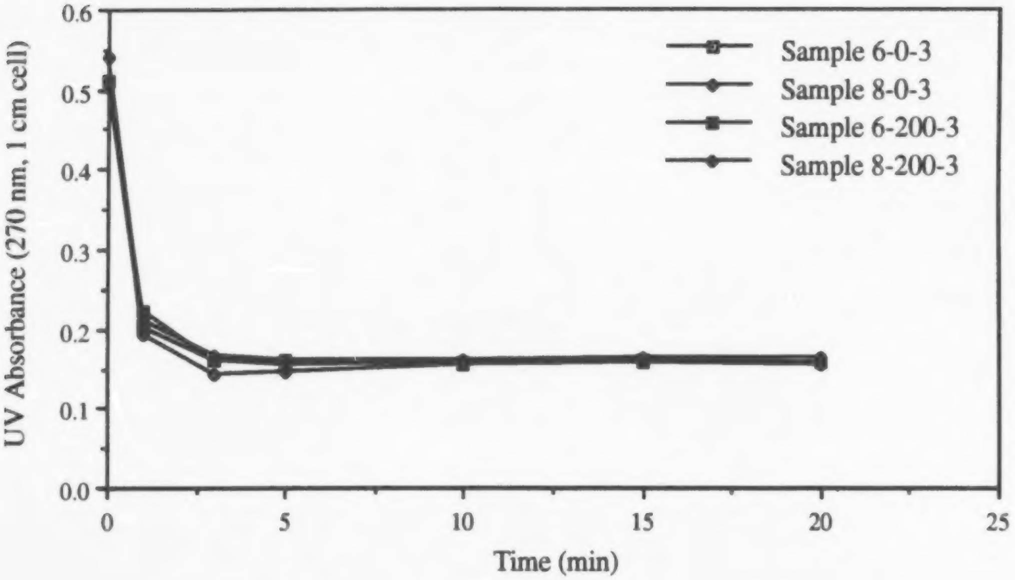


Figure 3.4 Change in Post-Ozonation UV Absorbances of Four Samples of Lakewater with Time. All at 20 mg/L NVDOC; 6,8 = pH 6, 8; 0,200 = 0, 200 mg/L Alkalinity as $CaCO_3$; 3 = 3:1 Ozone:NVDOC Ratio Employed

post-ozone chlorination and chloramination, methods for which are discussed in Section 3.3.4.

3.3.4 Post-Ozone Chlorination and Chloramination

Halogenated disinfection by-product formation potentials (XDBPFPs) were determined on selected ozonated and non-ozonated samples. Samples were measured into 150 mL bottles with Teflon®-lined caps and appropriate volumes of chlorine were added to achieve a 3:1 molar ratio of chlorine or chloramine to NVDOC. When chloramine was the oxidant used, ammonium chloride was added to the bottles before sample addition to achieve a 3 to 1 mass ratio of chlorine to ammonia. Preliminary testing showed that within 1 minute after mixing there was no detectable free chlorine in chloraminated samples. Samples remained at the pH at which they were ozonated for the test. They were incubated at room temperature and in the dark for 1 week before chlorine and chloramine residuals (amperometric titration, Standard Methods, APHA-AWWA-WEF, 1992) and XDBPFPs (described in the next section) were determined.

3.4 Disinfection By-Products Analyses

All DBPs were determined by gas chromatographic methods. Some method development details are included herein for techniques which were significantly altered from published protocols. Otherwise, more complete details regarding methods development can be found in Appendix I.

3.4.1 Ozonation By-Products

Ozonation by-products determined included the aldehydes, oxoacids and carboxylic acids listed in Table 3.3. Methodology schematics and typical calibration curves for each of the DBPs are given in Appendix I. Samples for these disinfection by-products analyses were taken either within 3.5 minutes (for experiments at 20 mg/L NVDOC) or following a

Table 3.3 Ozonation By-Products

Class	Compound
Aldehydes	Formaldehyde
	Acetaldehyde
	Glyoxal
	Methyl glyoxal
Oxoacids	Pyruvic acid
	Oxalacetic acid
	Glyoxalic acid
	Ketomalonic acid
Carboxylic Acids	Formic acid
	Acetic acid
	Propanoic acid
	Benzoic Acid

10 minute reaction period after stopping ozonation. Final measurement of all of the derivatized analytes was by gas chromatography with electron capture detection (GC/ECD).

Unfortunately, dicarboxylic acids such as oxalic acid could not be included because they were not amenable to the methods described below, and other equipment necessary for their analysis only became available after this work had nearly been completed. Similarly, phenols could not routinely be determined because of limited equipment availability.

3.4.1.1 Aldehydes

Aldehydes were derivatized by oximation with O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBOA; Aldrich) as described by Sclimenti *et al.* (1990) and analyzed by GC/ECD. A 20 mL aliquot of sample was added to a 40 mL EPA vial (Fisher Scientific Ltd.) containing 1 mL 6 mg/mL PFBOA. The vial was capped and heated at 45 °C for 2 hours. After cooling (30 min), the sample was acidified with 4 drops concentrated sulfuric acid and the derivative was extracted with 4 mL hexane containing 100 μg/L dibromopropane internal standard. The extract was washed with 10 mL 0.1 M sulfuric acid and then transferred to an autosampler vial containing approximately 20 mg sodium sulfate.

The oxime derivatives were analyzed by GC/ECD using a DB-5.625 capillary column (J&W Scientific; 30 m x 0.25 mm x 1.0 μm thickness) utilizing helium carrier gas at 1 mL/min (150 °C) and 5% methane in argon make-up gas at 25 mL/min. The injector temperature was 250 °C and the detector temperature was 300 °C. The oven was temperature programmed from 100 °C (held for 5 min) to 295 °C at 10 °C/min and held at the maximum temperature for 5 min. The sample injection volume employed was 2 μL, split 1:1.

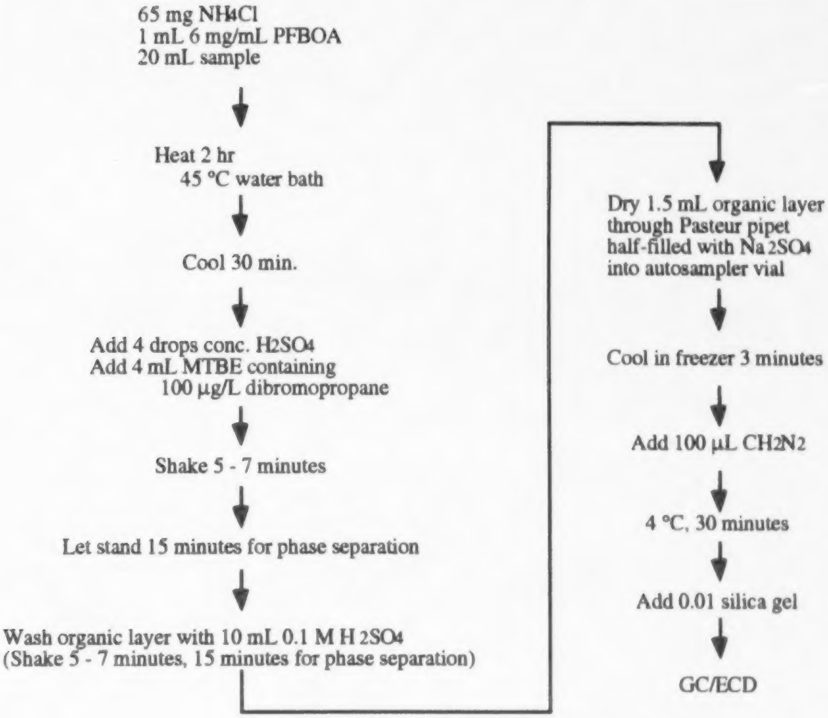
The concentration of aldehydes in a sample were determined from calibration curves prepared over a representative concentration range. Peak areas of the oximes were not measured relative to that of the internal standard. Typical calibration curves obtained are shown in Appendix I along with data illustrating analyte recoveries.

3.4.1.2 Oxoacids

Oxoacids were derivatized by a combined oximation-methylation procedure utilizing O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBOA) and diazomethane as outlined in Figure 3.5. While this research was in progress, similar methods were reported by other researchers (for example, Xiong *et al.*, 1992; Xie and Reckhow, 1992). The procedure first involved derivatization of the aldehyde or ketone functionalities of the compounds with PFBOA as described in Section 3.4.1.1. After acidification of the cooled samples with 4 drops of concentrated sulfuric acid, these derivatives were extracted with 4 mL methyl-t-butyl ether (MTBE) containing 100 μg/L dibromopropane internal standard. MTBE was found to be preferable to hexane (used by Xiong *et al.*, 1992) as an extracting solvent in that greater recoveries of the analytes could be realized. The extracts were washed with 10 mL 0.1 M sulfuric acid and then dried by passing them through Pasteur pipets half-filled with sodium sulfate. 1.5 mL of the derivatives were transferred to autosampler vials, cooled to ≤ 0°C and reacted with 100 μL diazomethane in diethyl ether for a minimum of 30 minutes at 4 °C. Excess diazomethane was then quenched with 20 mg silica gel, and the derivatized extracts were analyzed by GC/ECD.

3.4.1.3 Carboxylic Acids

Carboxylic acids were derivatized by extractive alkylation using dicyclohexylcarbodiimide and pentafluorophenol, a procedure adapted from that described by Wong *et al.* (1988). The method is illustrated in Figure 3.6. Unfortunately, this method did not allow for the analysis of oxalic acid or other dicarboxylic acids known to be ozonation DBPs because of decomposition of the derivatives in the injection port of the gas chromatograph.



GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 250 °C, detector 300 °C
oven: 100(5)-10-295(5)

Figure 3.5 Schematic Illustrating Methodology for Determining Oxoacids

20 mL sample
1 mL pH 6 buffer
400 μL 500 μg/L MBA I.S.
1000 μL 10 mg/mL TBAHS
3 mL Toluene
150 μL 2.5 mg/mL PFP
150 μL 2.5 mg/mL DCC

↓

Heat 70 °C 3 hours

↓

Let stand 30 minutes to cool

↓

Transfer organic layer to autosampler vial(s)

↓

GC/ECD

GC/ECD:

30m x 0.25mm x 1μm DB-5 capillary column
2 μL injection, split 1:1
injector 220 °C, detector 300 °C
oven: 90(5)-10-295(5)

Figure 3.6 Schematic Illustrating Methodology for Determining Carboxylic Acids

Briefly, it involved the aqueous derivatization of carboxylic acids in 20 mL sample with pentafluorophenol using dicyclohexylcarbodiimide as a coupling reagent, tetrabutyl ammonium hydrogen sulfate (TBAHS) to improve phase-transfer and 3 mL toluene as the extracting solvent. Mucobromic acid, 25 µg/L, was used as an internal standard. Samples were heated to 70 °C for 3 hours and cooled for 30 minutes before the organic layer was transferred to autosampler vials for GC/ECD analysis.

The derivatives were measured by GC/ECD using a 30 m x 0.25 mm x 1.0 µm DB-5.625 capillary column, using the same conditions as for aldehydes analysis except that the initial oven temperature was 90 °C instead of 100 °C. Carboxylic acid concentrations were determined from their peak areas and relevant calibration curves (shown in Appendix I).

This procedure was modified from that reported by Wong *et al.* (1988) which was used to determine carboxylic acids in human urine, and because it is a relatively new procedure, more details regarding development of the method will be given here than have been included for other analytes. Considerations made during the adaptation included those for differences in sample ionic strength from drinking water and urine (which might affect extraction efficiency and phase transfer catalysis), temperature effects (reaction kinetics at different temperatures, and differences in expected carboxylic acids concentrations (low µg/L *vs* low mg/L). Optimal pH was not explored as the pH used had been reported to be effective, however future investigations into altering the method might include this aspect of the reactions involved.

The rate of the reaction varied with the ionic strength of the solutions, but this effect was minimized by the addition of the ion pairing reagent tetrabutylammonium hydrogen sulfate. This is illustrated for acetic acid in Figures 3.7 and 3.8. Similar effects were noted for the other carboxylic acids tested and are shown in Appendix I. Also shown in Appendix I are results of similar experiments in which sodium sulfate alone was used to modify the ionic strength. From these experiments it was determined that the TBAHS

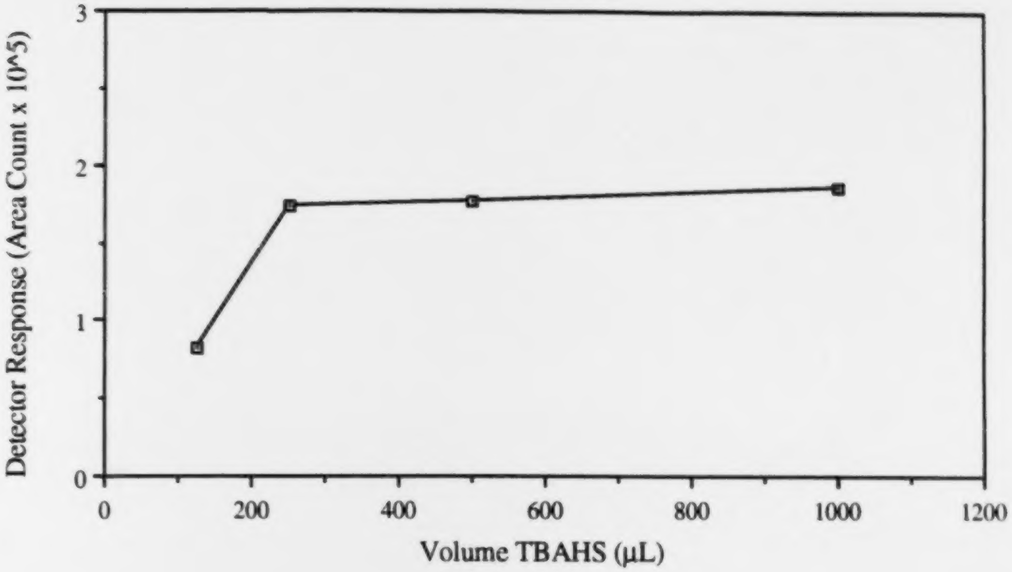


Figure 3.7 Effect of Tetrabutylammonium Hydrogen Sulfate Concentration on the Formation of Pentafluorophenol Ester of Acetic Acid (TBAHS=10 mg/mL, no added sodium sulfate)

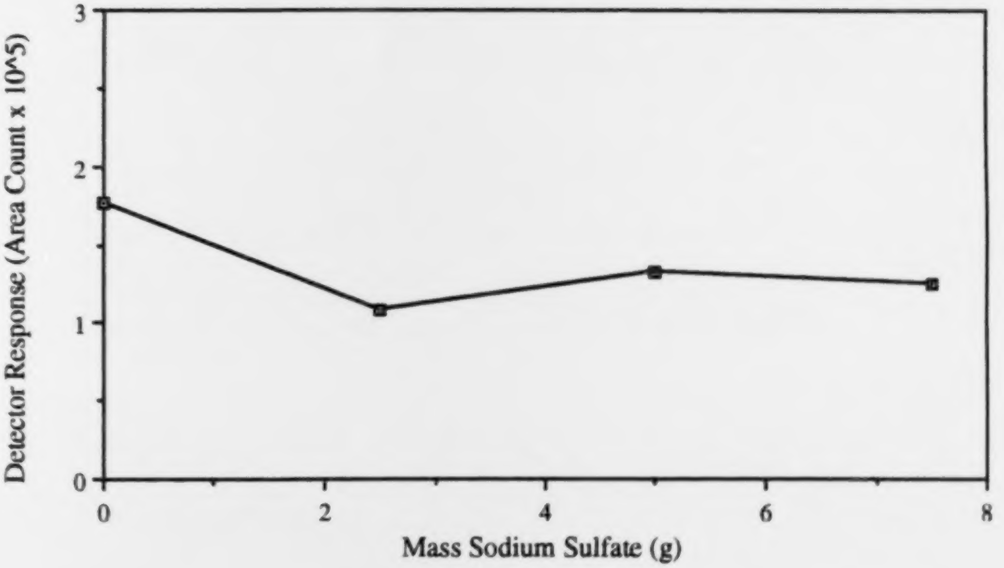


Figure 3.8 Effect of Salt Concentration on the Formation of Pentafluorophenol Ester of Acetic Acid in the Presence of 0.5 mg/mL TBAHS.

could be used without added ionic strength (sodium sulfate) if the concentration of TBAHS was 0.25 mg per mL sample or higher.

Reaction kinetics were studied at three temperatures: room temperature (nominally 20 °C), 45 °C and 70 °C. The samples reacted at room temperature were vortex mixed at 250 rpm to facilitate phase transfer, whereas those at the elevated temperatures were not mixed. The higher temperatures were tried because they would be expected to increase reaction rates and possibly product yields, and also because their use would make joint use of the water baths easier among the various research groups. These samples were not shaken because the water bath did not have a shaker. The results of these tests are shown in Figure 3.9 for acetic acid and in Appendix I for the other carboxylic acids investigated. They indicated that if a reaction temperature of 70 °C was employed, the derivatization appeared to be complete within approximately 3 hours. Therefore, a 3 hour reaction time at 70 °C was employed in the ozonation factorial experiments for the analysis of carboxylic acids.

Further information including calibration curves are included in Appendix 1. High concentrations of formic and acetic acids in method blanks (also illustrated in the calibration curves shown) were not uncommon. Attempts to reduce these concentrations were largely unsuccessful, and further work to this end would be beneficial. However, while these high concentrations could not be avoided they could be effectively accounted for by applying apropriate QA/QC protocols in the experimental plan (for example, by including blanks and spikes). In addition, absolute yields of the derivatized carboxylic acids were not determined in this study due to the unavailability of commercial standards and lack of time for synthetic work. Regardless of the actual yields of derivatives obtained, the method was reproducible under the conditions used, and provided satisfactory method detection limits (Appendix I).

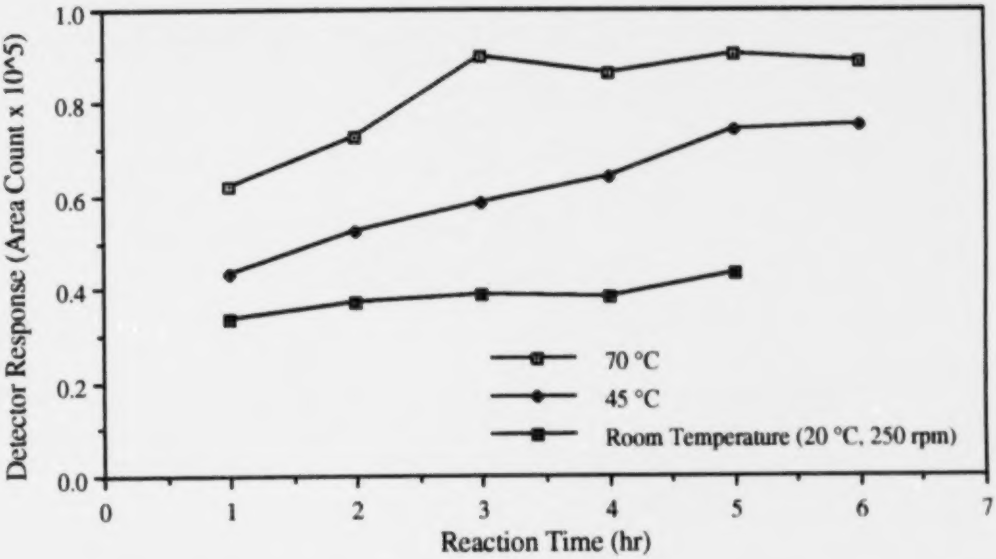


Figure 3.9 Kinetics of Formation of Pentafluorophenol Ester of Acetic Acid

3.4.2 Chlorination and Chloramination By-Products

Halogenated disinfection by-products (XDBPs) determined were the trihalomethanes (THMs), haloacetic acids (HAAs), chloral hydrate and cyanogen chloride listed in Table 3.4. Concentrations of these XDBPs represented their formation potentials under the conditions employed.

At the end of the 7 day incubation time, chlorine and chloramine residuals were determined by amperometric titration (Standard Methods) and samples were measured headspace-free into 40 mL EPA vials (Fisher Scientific) containing appropriate preservative for each of the analyses (Krasner *et al.*, 1989). These vials contained either ammonium chloride (65 mg) to preserve samples for THM and HAA analyses, or ascorbic acid (20 mg) for cyanogen chloride and chloral hydrate samples, as recommended by Krasner *et al.* (1989). They were filled headspace-free, capped with Teflon®-lined caps and then inverted several times to mix with the preservative. Cyanogen chloride samples were analyzed immediately, the remaining preserved samples were stored at 4 °C in the dark and analyzed as soon as possible within the recommended sample holding times (Appendix I, Krasner *et al.*, 1989).

Methods used for XDBPs were as described by Krasner *et al.* (1989) or Koch *et al.* (1991) with minor modifications, except for cyanogen chloride, as described in Section 3.4.2.1. References for and/or a brief description of each method are described herein. All XDBP analyses were performed using an HP-5790A gas chromatograph with a 30 m x 0.25 mm I.D. DB-5.625 capillary column (1 µm film thickness, column head pressure 12 psi) and electron capture detector. Injection of 2 µL sample extract was performed by autoinjector. Detection limits and further information for the XDBPs determined in this study are shown in Appendix I.

Table 3.4 Halogenated Disinfection By-Products

Class	Compound
Trihalomethanes	Chloroform
	Dichlorobromomethane
	Dibromochloromethane
	Bromoform
Haloacetic Acids	Dichloroacetic acid
	Trichloroacetic acid
Miscellaneous	Chloral hydrate
	Cyanogen chloride
	Chloro-oxoacids
	Chlorophenols

3.4.2.1 Cyanogen Chloride

A salted liquid-liquid extraction procedure followed by gas chromatographic separation and electron capture detection (GC/ECD) was used for the determination of CNCl. This method was recommended by West (1992) and is similar to that for THMs (Krasner *et al.*, 1989, described below) except that cyclohexane was used instead of pentane because it produced a better chromatographic baseline than did pentane. Extracts were analyzed by GC/ECD isothermally at 35 °C (injection port 157 °C, detector 300 °C). Equipment problems prevented use of the standard purge-trap-GC/MS method, however the solvent extraction method proved to be simple and sensitive (0.1 µg/L detection limit).

Again, because this was a relatively new technique, additional information regarding methods development is warranted herein. The data in Figure 3.10 shows that there is a significant effect of ionic strength on cyanogen chloride recovery. However, at the concentration of sodium sulfate employed in the test (5 g/sample), the effects of ionic strength had reached a maximum and further variations would be minimal.

3.4.2.2 Trihalomethanes

THMs and THMFPs were determined by the salted pentane extraction method described by Krasner *et al.* (1989) with only minor modifications. Prior testing compared purge and trap results to those obtained with this method and found them to be comparable. The GC used does not have cryogenic capability, necessitating the use of a different temperature program for separation of sample components than that specified in the literature. The GC oven temperature program was: initially 50 °C, hold 5 min then program at 5 °C/minute to 250 °C and hold 5 min. Preliminary testing showed that component resolution without the cryogenics was still more than adequate and enabled detection limits below 1 µg/L to be obtained for the THMs.

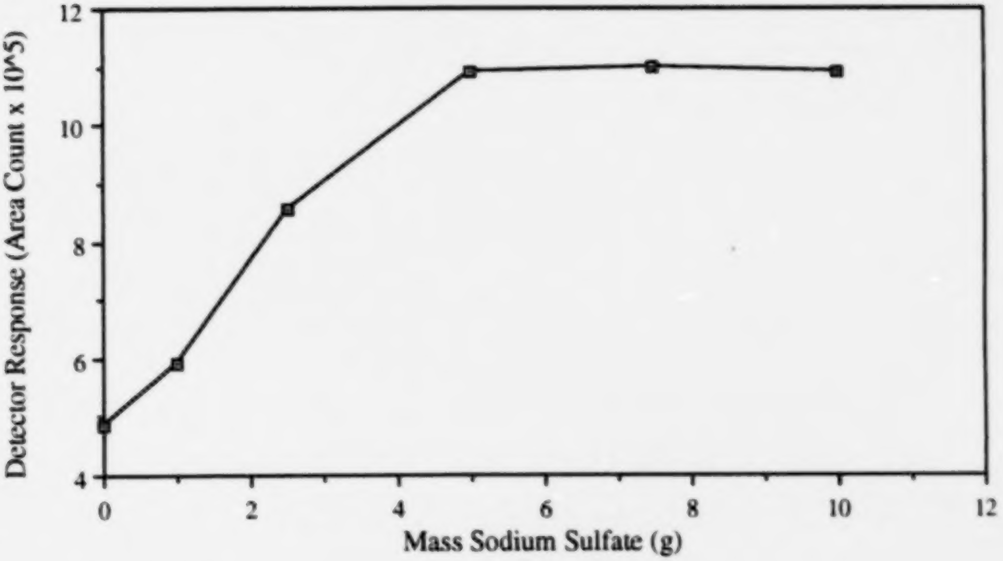


Figure 3.10 Effect of Ionic Strength on Cyanogen Chloride Extraction Efficiency

3.4.2.3 Haloacetic Acids

Acidic, salted methyl-t-butyl ether (MTBE) extraction and diazomethane derivatization were used to determine HAAs and HAAFPs. The method was similar to that described by Krasner *et al.* (1989) but was simplified as shown in Appendix I and utilized bromoacetic acid (BrAA) and 1,3-dibromopropane as internal standards instead of 2,3-dibromopropionic acid and 1,3-dibromopropane. Briefly, 20 mL sample containing 10 µg/L BrAA surrogate internal standard was extracted with 4 mL MTBE containing 1,3-dibromopropane internal standard after acidification with 1.5 mL concentrated sulfuric acid. The extract was dried over sodium sulfate crystals in Pasteur pipets, and 1.5 mL was methylated with 200 µL freshly prepared diazomethane at 4 °C for a minimum of 0.5 h. After quenching the remaining diazomethane with 20 mg silica gel, the extract was analyzed by GC/ECD using the following conditions: initial temperature 50 °C, hold 10 min then program at 5 °C to 250 °C and hold 5 min (injection port 157 °C, detector 300 °C).

3.4.2.4 Chloral Hydrate

Chloral hydrate was determined by the salted methyl-t-butyl ether (MTBE) extraction method described by Krasner *et al.* (1989), and employed the same GC conditions as for THM analysis. The conditions differed from those used by Krasner et al. because the gas chromatograph used did not have cryogenic capability, however good peak resolution and chloral hydrate detection limits were obtainable. Typical calibration curves are shown in Appendix I.

3.4.2.5 Chloro-oxoacids and Chlorophenols

Selected samples were analyzed for oxoacids exactly as described in Section 3.4.1.2, but are termed chloro-oxoacids here because the samples had undergone chlorination or chloramination and it was the chlorinated analogs that were of interest. The compound 3-chloro-4-(dichloromethyl-5-hydroxy-2(5H)-furanone, also known as MX, could be determined by this method, and chlorinated phenols could also be detected. Only qualitative determinations were possible because of the lack of a good quality quantitative standard.

3.5 QA/QC

In the following sections are described the means by which the quality of data appearing in subsequent chapters was assured or ascertained. They relate to all aspects of the present research, including the quality of reagents used, means to determine the quality of NOM isolated, experimental details relating to aspects of the ozonation procedures which affected the quality of the results, and to QA/QC associated with the individual analytical methods employed.

3.5.1 Reagents

The resistivity of the water from the Milli-Q® treatment system was checked before use. It was considered acceptable for use if it was greater than 10 µmho. Alkaline permanganate distillation was attempted to improve the levels of aldehydes determined in blanks, but proved to be too time consuming for the minimal increase in purity obtained.

Indigo trisulfonate solutions for the determination of ozone residuals were prepared and periodically replaced according to criteria described in Standard Methods (1992).

Immediately prior to use in adsorption or desalting columns, XAD and ion exchange resins were eluted with Milli-Q® water and the effluents were monitored for NVDOC concentration. When the effluent NVDOC concentration was less than 0.5 mgC/L, the resins were considered to be free of contamination from solvents used in their initial cleaning.

3.5.2 NOM Isolation

Samples were obtained prior to the addition of any chemical, and upstream of urban inputs (for river water). They were acidified and cooled to 4 °C immediately to prevent deterioration.

With regard to filtration, adsorption to the filtration membranes was determined experimentally to be insignificant. NVDOC measurements before and after filtration were within experimental error of each other. Also, all samples were filtered at room temperature to ensure consistent filtration efficiency. Sample portions were warmed to room temperature and filtered as needed. The pHs of acidified raw sample and filtered samples were determined to be within experimental error of each other.

The adsorption process was monitored as described in Sections 3.2.3 and 3.2.8. All water-contacting surfaces were constructed of stainless steel, Teflon®, Viton® or glass to reduce the possibility of contamination. In addition, sample flow rates were checked daily by timed measurement of effluent into a graduated cylinder.

The desorption process was checked by performing a mass balance. NVDOC concentrations and corresponding sample volumes were used to compare sample organics concentrations and the yields of lyophilized NOM as shown in Appendix II. The yields obtained were in general agreement with those reported by others for similar materials (Malcolm, 1991; Leenheer, 1981).

After initial separation of humic and fulvic acid fractions, the NOM solutions were left overnight at 2 °C to determine if additional precipitate would form. See Section 3.2.5 for more details.

Desalting procedures were checked by the monitoring efforts described in Section 3.2.6.

3.5.3 NOM Characterization

UV absorbance measurements were made with the same 1 cm cells throughout this research, and the spectrometer was zeroed with Milli-Q® water prior to each use.

Much of the other NOM characterization was performed by others as is indicated in Section 3.2.9. Quality control practices employed in those laboratories may be provided on request.

3.5.4 Ozonation Experiments

Both phosphate and borate buffer systems were tested for ozone scavenging potential prior to NOM experiments. As is described in Appendix I, borate was an appreciable ozone scavenger, but phosphate buffered solutions were able to hold an ozone residual. Therefore, phosphate buffers were used.

Prior to NOM ozonation, the NVDOC of the test solutions was confirmed by measurement (Xertex Dohrmann DC 80 Total Carbon Analyzer).

The pH of the test solutions was determined before and after ozonation to confirm the effectiveness of the buffer system.

Ozone-demand-free water was used for the experiments (see Section 3.1 for preparative details).

Gaseous ozone concentrations were determined by potassium iodide trap and sodium thiosulphate titration prior to ozonation testing. The flow rate of gaseous ozone through the contactors was confirmed at ± 2 mL/min using a gas flow meter. Ozone-contacting surfaces were non-reactive and were made of either glass or stainless steel, except for the pump tubing which was silicone.

Ozonation timing was controlled manually by stopwatch. Timing was started when bubbles appeared from the porous glass diffuser and was stopped when the diffuser was removed from solution at the end of the specified ozonation time.

The order in which the NOM solutions were ozonated was randomized by selecting numbered pieces of paper from a beaker. This was necessary to remove determinate error from the factorial design.

Factorial midpoints were prepared and ozonated in triplicate to provide an estimate of the random error associated with each factorial data point.

3.5.5 DBPs Analyses

Reagent blanks using Milli-Q® grade water were included in each set of DBP analyses, and a raw water blank was included for each set of raw water samples tested.

At least one standard was prepared and analyzed for each analyte for each set of ozonation experiments or XDBP formation potential determinations. The concentration determined was to be within 5 % of the expected value.

Selected samples were spiked with standard analyte to estimate possible matrix effects on analyte recovery. One spike was performed for each raw water ozonated (and post-chlor(am)inated), and selected fulvic acid solutions were also spiked. Initial determinations with the fulvic acid solutions provided acceptable recovery data (typically greater than 95 %) so these spikes were not always performed.

Factorial experiment midpoints were prepared in triplicate to determine the uncertainty in the results and enable quantitative judgements regarding the observed effects to be made.

Most of the analyses employed internal standards to either improve quantitation reproducibility or to determine GC detector stability. These are listed in the sections relevant to the individual methods, and in Appendix I. The analysis for cyanogen chloride did not employ an internal standard as an appropriate one could not be found in the time given; however, sample recoveries and reproducibility as determined by external standard were acceptable. Should the method for cyanogen chloride described in this thesis be adopted by others, it would be prudent to identify and use an appropriate internal standard.

Of the internal standards used, only that for the determination of haloacetic acids (bromoacetic acid) was used directly for calculations of analyte concentration. Calibration curves of area ratio of analyte to bromoacetic acid *vs* analyte concentration were used to quantitate the haloacetic acids. In all other instances, analyte concentrations were determined from calibration curves of peak area *vs* analyte concentration, and the internal standard was used to determine GC-ECD stability.

Standard curves were prepared every 2 to 4 months, even if check standards performed as part of the experimental protocol provided acceptable concentration data.

Extraction solutions were prepared fresh with each ozonation experiment or XDBP formation potential test, or were replaced every 2 weeks.

Stock solutions of analyte standards were replaced if their concentrations decreased by approximately 10 %, or were prepared every 2 to 4 months.

Detection limits for each of the analytes were determined in the lab under the conditions of extraction and derivatization to be used in experiments.

Analytical precision for each DBP was determined in reagent grade water prior to tests, but during the tests selected individual samples were analyzed in triplicate to obtain the precision for the analysis under the experimental conditions. Expense, time and equipment limitations prevented analysis of all samples in triplicate, however since the procedures involved determining DBPs for similar samples several times, the repetition of each individual analysis was less important. Analytical precision data determined in reagent grade water and in samples were comparable and typically had values of less than 5% RSD.

CHAPTER 4

ISOLATION, FRACTIONATION AND CHARACTERIZATION OF NOM FROM RIVER WATER AND LAKEWATER

One of the major problems in studying specific aspects of environmental processes such as the production of disinfection by-products (DBPs) during drinking water treatment is that sample matrices are complex, making specific cause and effect relationships difficult to determine. Another is that DBP samples may be dilute and formation of species of interest may occur near analytical detection limits. Isolation procedures such as those employed in this research provide at least partial answers to some of these problems. The humic and fulvic acids, possible precursors for the DBPs being studied, can be separated from the bulk of the natural organic matter (NOM) and inorganic matrix and as such may be evaluated without the possible complications of matrix involvement. The procedure enables one to select reactant concentrations as desired, even at higher concentrations than normally encountered, to enhance DBP detection. In addition, it provides a means to further classify NOM into operational categories, making cause and effect relationships easier to study and precursor identities easier to define. While the extent to which the isolation procedure itself alters the nature of the NOM is unknown, the procedure allows the aforementioned problems to be reduced for study purposes.

What follows are descriptions of the calculations and preliminary experiments performed to evaluate efficiency of the isolation process, water quality data for samples, analysis of the data obtained during monitoring of the isolation procedure and the characteristics of the resulting NOM fractions.

4.1 Resin Capacity Calculations and Tests

Researchers who study aquatic NOM on a regular basis often obtain their test materials using large-scale isolation apparati (Malcolm, 1991) which is typically unavailable in many laboratories. Calculations and preliminary tests were required to determine if equipment available in our laboratory would be adequate for the isolation procedure.

First, using data presented by Malcolm (1991) and knowledge of typical levels of DOC in the source waters, sample volumes that would be required to obtain desired quantities of humic and fulvic material were estimated. Malcolm (1991) states that while as little as 50 mg material is required for complete characterization, a more practical minimum amount is 100 to 200 mg. Therefore, 300 mg was selected to be the minimum quantity of NOM to obtain in each sampling. This would allow for 100 mg to be used for characterization and the remaining 200 mg material for ozonation experiments. Malcolm (1991) also indicates that typically 45 % of DOC is composed of fulvic acids, and that the concentration of humic acids is only one ninth that of the fulvics concentration. Assuming a conservative recovery of 80% and an influent DOC of 2 mg C/L (the lowest anticipated), the largest volume of sample required was calculated to be:

$$\begin{array}{c}\text{Maximum sample volume for}\\ \text{300 mg fulvics}\end{array} = \frac{300\ \text{mg}}{2\ \text{mg/L} \times 0.4 \times 0.8} = 470\ \text{L}$$

$$\begin{array}{c}\text{Maximum sample volume for}\\ \text{300 mg humics}\end{array} = 9 \times 470\ \text{L} = 4200\ \text{L}$$

Assuming a sample DOC of 2.5 mg C/L, which represents a typical concentration for North Saskatchewan River water, the required volumes were reduced to 375 L and 3375 L, respectively. For the lakewater sample location, assuming a DOC of 15 mg C/L, 62.5 L and 562.5 L were required to isolate 300 mg fulvic and humic material, respectively. These quantities agreed with examples presented by Malcolm (1991) where 400 mg of fulvic acids were calculated to require 275 L of a sample with DOC of 4.5 mg C/L. To isolate 400 mg humic acids from the same sample, 2250 L were required.

Considering the available sampling equipment (330 L per run) and the above assumptions, it was theoretically possible to obtain the following NOM fractions:

$$\text{North Saskatchewan River fulvic acids} = 2.5 \text{ mg C/L} \times 330 \text{ L} \times 0.4 \times 0.8 = 270 \text{ mg C}$$

$$\text{North Saskatchewan River humic acids} = 2.5 \text{ mg C/L} \times 330 \text{ L} \times 0.4 \times 0.8/9 = 30 \text{ mg C}$$

$$\text{Driedmeat Lake fulvic acids} = 15 \text{ mg C/L} \times 330 \text{ L} \times 0.4 \times 0.8 = 1580 \text{ mg C}$$

$$\text{Driedmeat Lake humic acids} = 15 \text{ mg C/L} \times 330 \text{ L} \times 0.4 \times 0.8/9 = 170 \text{ mg C}$$

Not considered in these calculations are the chromatographic effects described by Malcolm (1991), discussed below, which affect the amount of sample that can be processed prior to resin regeneration.

To determine if the chromatographic properties (described by k' below) of the organics in the source waters chosen were similar to those reported by Malcolm (1991) and confirm the appropriateness of the above calculations, breakthrough data were obtained using acidified and filtered samples of the two source waters under consideration. Two small glass columns (approx. 10 mm dia. x 200 mm) were filled with 10 mL each of cleaned XAD-8 resin and used to adsorb NOM from approximately 400 mL sample. According to the following relationship:

$$V_e = V_o (1 + k') \tag{4-1}$$

Where:

V_e = breakthrough elution volume

V_o = column void volume

k' = column capacity factor

$$k' = \frac{\text{(mass solute sorbed)}}{\text{(mass solute dissolved)}}$$

with V_o = 5 mL, and k' = 50 considered minimal for these types of surface waters, then the amount of sample throughput possible to 50% breakthrough should have been 255 mL.

The sample flow rate employed was the recommended 5 to 10 column volumes per hour (approximately 1 mL/min). Samples were collected at 20 to 30 mL intervals for DOC analysis.

Results of these preliminary tests are shown in Figures 4.1 and 4.2. What appears to be immediate breakthrough is the passage of relatively unadsorbed hydrophilic organic matter through the column. Malcolm (1991) reported that approximately 40% of the DOC was actually this hydrophilic fraction, as is shown in Figure 4.3 which illustrates an idealized breakthrough curve (Malcolm and MacCarthy, 1992). NVDOC concentrations for test samples were 17.2 mg C/L for the lakewater and 4.3 mg C/L for the river water. Continual breakthrough of approximately 1.8 and 9.2 mg C/L represented hydrophilic components comprising 53 and 42% of the sample DOC, respectively, and therefore agreed with estimates provided by Malcolm (1991). Breakthrough of fulvic material was not observed during the course of this experiment, even when using the high DOC sample.

Figure 4.4 is a representation of the end result of the experiment. 400 mL of 4.3 mg C/L river water caused only a slight discolouration in the top 5 mm of the 108 mm length column. The high DOC lakewater resulted in discolouration of the top 20 mm of resin, of which the top 5 mm was more darkly and uniformly coloured. It was assumed that the uniformity and darkness of the top 5 mm of the column used for the lakewater sample indicated maximum adsorption and the next 15 mm represented the DOC wavefront (7.5 mm to midpoint of wavefront). The volume to breakthrough and k' were then:

$$\begin{array}{c}\text{Sample Volume to}\\ \text{0.5 Max Fulvics Breakthrough}\\ \text{for a 10 mL Column}\end{array} = (108\text{ mm} - 7.5\text{ mm}) * 400\text{ mL} = 4020\text{ mL}$$

and

$$k' = \frac{V_E}{V_O} - 1 \qquad (4\text{-}2)$$

$$k' = \frac{4020\text{ mL}}{5.2\text{ mL}} - 1 = 773$$

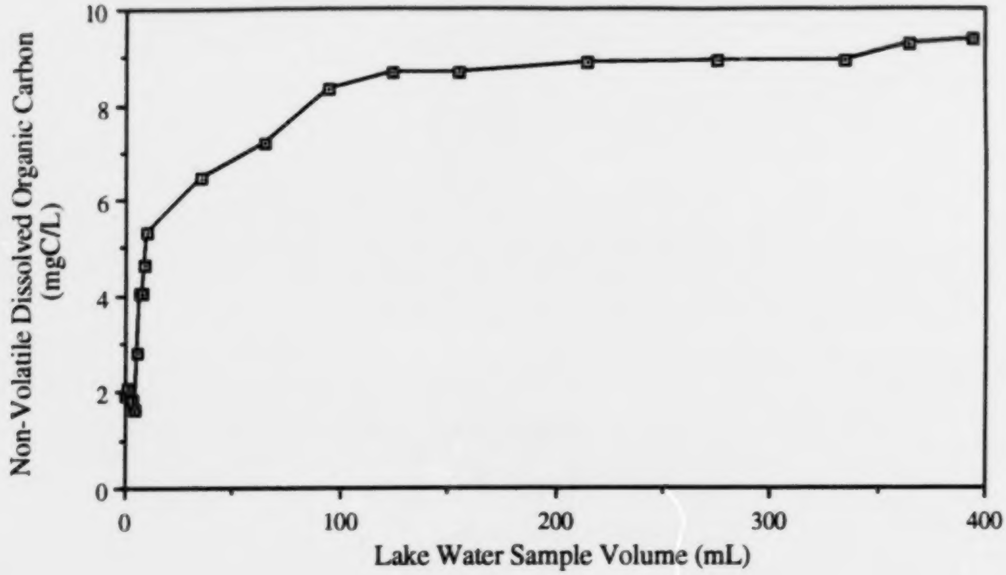


Figure 4.1 Preliminary Breakthrough Curve for Adsorption of NOM from Driedmeat Lake Water on XAD-8 Resin (17.2 mg/L DOC)

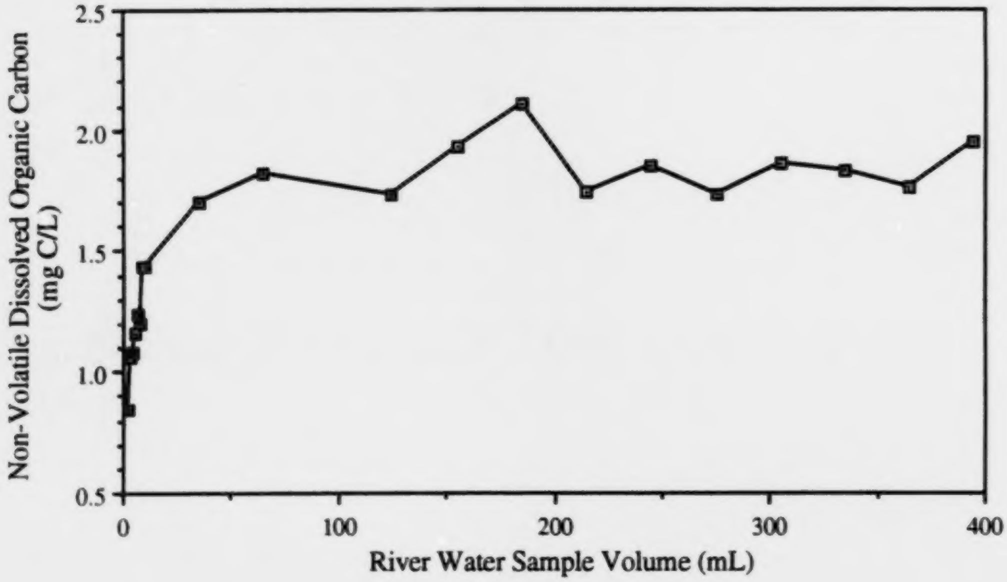


Figure 4.2 Preliminary Breakthrough Curve for Adsorption of NOM from North Saskatchewan River Water on XAD-8 Resin (4.3 mg/L DOC)

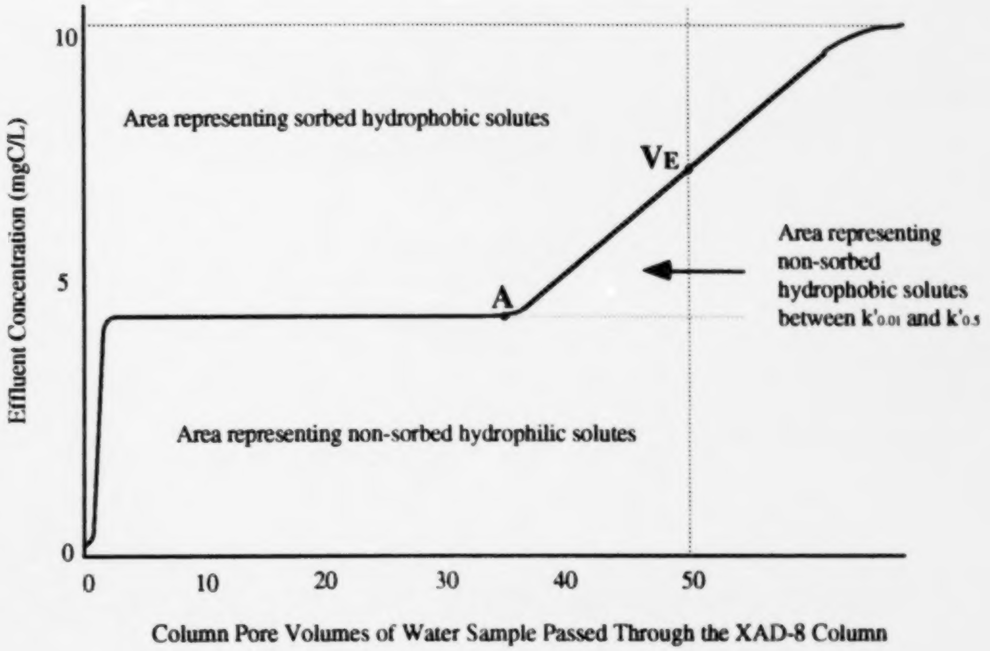


Figure 4.3 Idealized Breakthrough Curve for Stream Humic Substances on XAD-8 Resin. VE = sample volume for $k'_{0.5}$ = 50. A = point of first detectable breakthrough. At VE, adsorption is stopped and elution is started. (Adapted from Malcolm and MacCarthy, 1992)

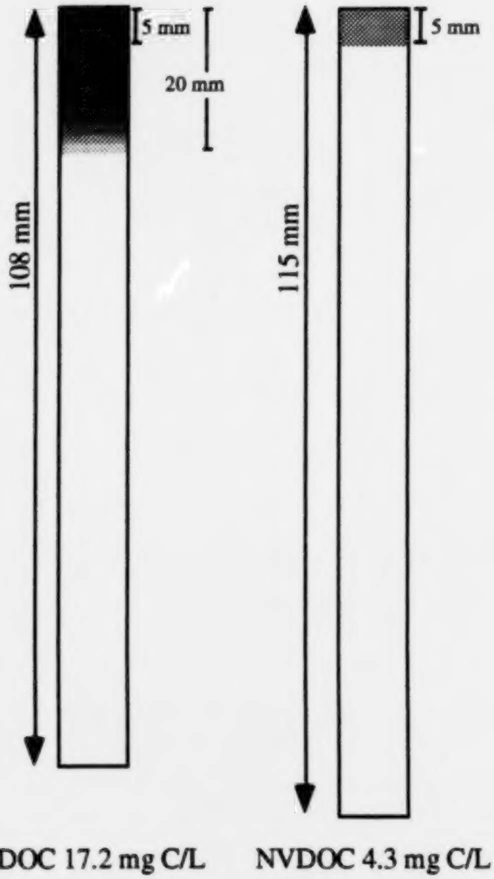


Figure 4.4 Extent of Breakthrough for 400 mL Test Water on 10 mL XAD-8 Resin Columns

The estimated value for k' of 735 was extremely large, considering the expected value was 50. It could not be used with confidence for predicting breakthrough of DOC in the larger adsorption columns during humics isolation for several reasons. Adsorption of uncoloured material could be occurring which would hasten the progression of the coloured band down the column with time and sample volume, and thereby result in a reduced k'. As well, uniform discolouration of the top 5 mm of resin may not indicate loading to capacity, in which case the k' value estimated above would be lower than the actual value. The main result of this experiment was that less resin was required than was predicted using the Malcolm (1991) calculations and/or it required regeneration at less frequent intervals. However close monitoring of the adsorption columns was required to ensure efficient operation.

4.2 NOM Isolation

In this research, NOM isolated from two surface water sources using XAD-8 resin followed by XAD-4, and later also using AG-MP 50 resin. One source was the North Saskatchewan River sampled at the main supply line to the E.L. Smith Water Treatment Plant in Edmonton Alberta. This source provided untreated surface water of relatively low organic concentration (typically 2 to 3 mg/L NVDOC). Consideration was given to using the supply line at the Rossdale Water Treatment Plant but the E.L. Smith site was chosen because of its location upstream of urban inputs to the river. The second site was that of a surface water which contained a much higher organic concentration (10 to 20 mg/L NVDOC). Driedmeat Lake supplies the City of Camrose Alberta with source water for its drinking water treatment plant. The lake is shallow, having an average depth of 2.2 m, and experiences problems in the summer months with algal blooms. Samples were collected during mid- to late September while DOC levels remained high, following completion of XAD resin preparation. Samples were obtained from a point prior to the pre-chlorination stage of the treatment plant to avoid contaminating samples with chlorinated material not normally present.

Samples were collected in glass carbuoys and acidified to pH 2 immediately upon return to the laboratory (maximum 4 hr delay). Several 19 L and 15 L carbuoys were used to provide a total sample capacity of 330 L. Samples were filtered through 1.5 µm glass prefilters and 0.45 µm Durapore® filters to remove particulates and bacteria prior to being passed over pre-cleaned XAD resins. As described in Chapter 3, the NOM was then desorbed, fractionated, desalted and lyophilized according to procedures outlined by Malcolm (1991).

4.2.1 Raw Water Quality Data

Water quality data for the two sources was obtained from utility reports and are listed in Table 4.1. In addition, pH, temperature, conductivity and UV absorbance data were collected on source water samples and post-resin fractions as part of the NOM isolation monitoring efforts. These data are presented where appropriate in sections of the text or in Appendix II.

4.2.2 Adsorption Monitoring Data

NOM breakthrough on the XAD resins was monitored by collecting effluent and analyzing for non-volatile dissolved organic carbon (NVDOC) and UV absorbance at 254 nm. Influent samples of each 200 to 300 L raw water batch were collected and analyzed at least three times during the adsorption process. Breakthrough monitoring for the ion exchange resins was initially conducted via conductivity and NVDOC measurements, however these both proved to be ineffective parameters. Later, sodium and potassium ion were monitored as described by Leenheer (1981) using flame photometry.

Typical adsorption monitoring data are shown in Figures 4.5 and 4.6, in which effluent concentrations are plotted relative to influent concentrations (C/C_0) to compensate

Table 4.1 Water Quality Data for Driedmeat Lake and the North Saskatchewan River at Edmonton*

Parameter	Driedmeat Lake	North Saskatchewan River**
Alkalinity, mg/L	260	122
Calcium, mg/L	84	117
Colour, TCU	55	2.2
Conductivity, µS/cm	316	261
Total Hardness, mg/L	156	167
pH	8.54	7.94
Temperature, °C	13.6	2.18
Turbidity, NTU	7.4	3.1
Phosphorus, µg/L	116.6	NA***
Total Dissolved Solids, mg/L	261	NA

*Source: City of Camrose and City of Edmonton Utility Summary Monthly Reports.
Sample Dates: Driedmeat Lake, Sept. 26, 1991
North Saskatchewan River, Dec. 13, 1991 to Feb. 21, 1992

** Mean of twelve samplings

*** NA = Not Available

for small variations in the chemical nature of individual batches of filtered water. Shown are data for filtered lakewater adsorption but river water adsorption data were similar. Immediate breakthrough of hydrophilic material through the XAD-8 resin was high, accounting for approximately 70 to 75 % of the influent NVDOC (Figure 4.5). When measured as UV-absorbing or coloured material, the hydrophilic portion constituted approximately 50 to 65 percent of the influent (Figure 4.6). The XAD-4 resin reduced the effluent NVDOC concentration by a further 15 % (of the XAD-8 effluent), and by approximately 25 % when measured as UV absorbing or coloured material.

The uniformity in the data shown in Figure 4.6 relative to that in Figure 4.5 indicates that measurement of UV absorbance was superior to NVDOC as an adsorption monitoring parameter. The UV data were not as subject to influences of changing water quality as were NVDOC data in that smoother breakthrough curves were obtained. NVDOC data near the end of the adsorption process indicated near total humics breakthrough whereas UV data remained constant at the steady state levels indicating that humics isolation was still occurring at approximately the same rate. If NVDOC had been the only measurement conducted, humics isolation may have been terminated earlier than required and resin regeneration may have been performed more often than necessary.

Some of the XAD-4 monitoring data appeared contrary to typical breakthrough curves in that they showed an initial decrease, rather than an increase in the amount of NVDOC breakthrough with time. This phenomenon was most likely attributable to bleed of residual methanol from the XAD-4 resin for the first several liters of sample throughput, although pre-test NVDOC measurements indicated that this should not have been a problem. Corresponding UV absorbance monitoring data supported this theory in that the breakthrough curve for each of the adsorption/ion exchange units were much more typical. Initial breakthrough values increased from the baseline rather than decreased from a positive value. It is expected that the main effect of the presence of methanol in this XAD-4 column would have been to reduce organics recoveries from that resin, and possibly from

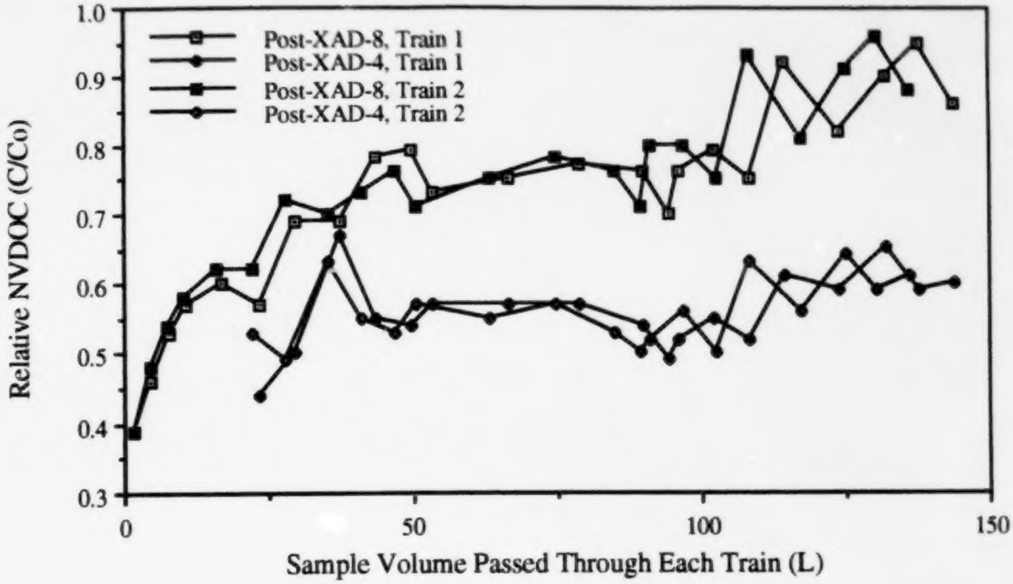


Figure 4.5 Non-Volatile Dissolved Organic Carbon Monitoring Data for Filtered Lakewater

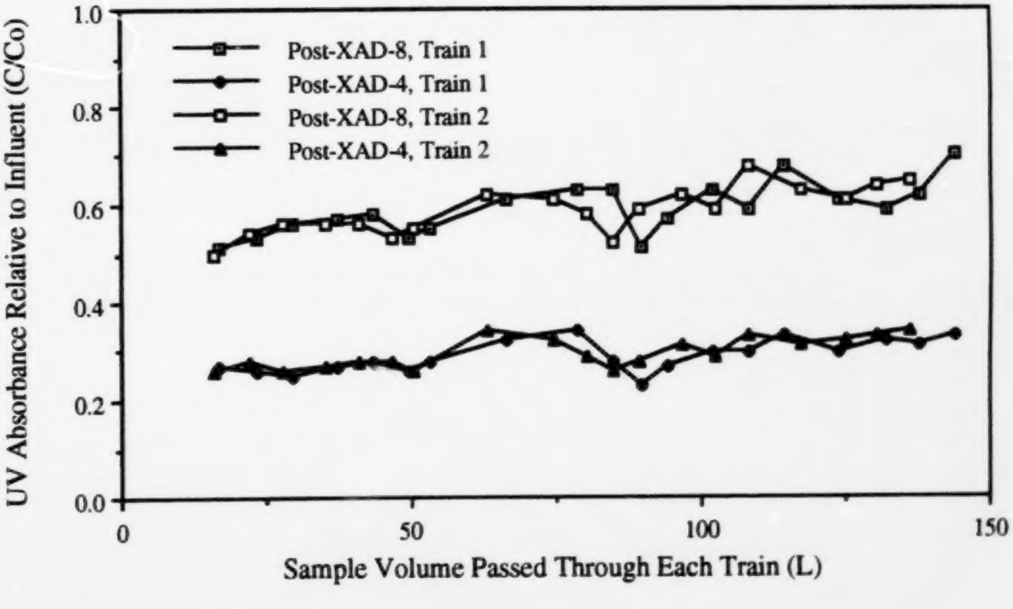


Figure 4.6 UV Absorbance Adsorption Monitoring Data for Filtered Lakewater

the subsequent ion exchange column, during that time rather than significantly affect the quality of the material subsequently desorbed. This observation underscored the value of UV as a monitoring parameter, and also showed that the UV and NVDOC measurements are complementary.

Significant breakthrough of humic or fulvic material above steady state levels, as indicated by UV measurements, was not observed during the course of the adsorption phase. As discussed previously, k' values estimated from this data for the humics on the XAD-8 column are very different than that reported by Malcolm (1991) for river water (greater than 700 as opposed to 50). However, other literature states that k' values of humic material of as great as 2000 are not uncommon (Thurman and Malcolm, 1981).

In summary, UV was found to be superior to NVDOC as an adsorption monitoring parameter because estimation of humics breakthrough using UV data was not as subject to the influences of changing water quality. However, UV does not detect problems such as the presence of high residual methanol concentrations in the adsorption columns resulting from incomplete resin preparation. Therefore, monitoring by UV and NVDOC measurements were shown to be complementary.

4.2.3 Fraction Yields

Yields of the various NOM fractions are shown in Table 4.2. Similar yields were obtained for the lakewater (300 L) and river water (2100 L) samples. Approximately equal masses of fulvic acids were obtained from XAD-8 and XAD-4 resins for each source. A total of 2.5 g of fractionated NOM was isolated from the river water samples and 2.6 g NOM was recovered from the lakewater. The freeze-dried river and lakewater humic and fulvic acids were similar in appearance to reference materials obtained from the International Humic Substances Society (IHSS, MacCarthy, 1992). Of the 2.5 g river water NOM, 118 mg were humic acids, 2.1 g were fulvic acids (1.1 g from XAD-8 resin and 1.0 g from XAD-4 resin), and 265 mg were hydrophilic bases (isolated by ion

Table 4.2 Mass of Freeze-Dried NOM Fractions Isolated from Driedmeat Lake and the North Saskatchewan River

	Yield (mg)	
Isolate Type	Driedmeat Lake	North Sask. River
XAD-8 Resin		
Humic Material	171	118
Fulvic Material	1265	1093
XAD-4 Resin		
Humic Material	0*	0**
Fulvic Material	1138	1004
AG MP-50 Resin		
Hydrophilic Bases	NA***	265
Hydrophobic Neutrals		
XAD-8 Resin	1240	2260
XAD-4 Resin	2260	2170

* Not isolable, estimated to be less than 10 mg.
** No precipitate detected on adjustment to pH < 1.0.
***Not applicable, fraction not obtained.

exchange). The fractions of the lakewater NOM included 171 mg humic acids, 1.3 g XAD-8 fulvic acids and 1.1 g XAD-4 fulvic acids. Relative amounts of humic and fulvic acid (approximately 9:1 or 10:1 fulvic to humic acids) agreed with quantities reported by Malcolm (1991). Considering the NVDOC of the lakewater and river water (approximately 15 and 1.5 to 2 mg C/L, respectively), it was apparent that the NOM recovery efficiencies from each source were comparable. A carbon balance was performed on the lakewater NOM showing that 47 % of the NVDOC could be considered as humic and fulvic acids, which agreed with figures reported by Malcolm (1991, Figure 1.2), and that the overall recovery of these components using the adsorption protocol was approximatley 70 % (Appendix II). Also, relative amounts of humic and fulvic acid isolated on XAD-8 were as expected (approximately 9:1 or 10:1 fulvic to humic acids (Malcolm, 1991; Xiong *et al.*, 1992), confirming that the isolation procedure were performed in a similar manner to that used by the IHSS.

4.2.4 Characterization of Fractions

In order to confirm the similarity of the isolated materials to those provided by the IHSS, and to enable possible relationships between DBP production and NOM characteristics to be explored, selected fractions were further characterized prior to ozonation experiments. NOM characterization data obtained from the IHSS are contained in Appendix III.

The river and lakewater NOM isolated on XAD-8 resin were similar in appearance and measured UV characteristics (Tables 4.3 and 4.4) to the IHSS reference materials. The IHSS materials were also obtained using an XAD-8 resin adsorption procedure similar to that used in this research. Relative amounts of humic and fulvic acid obtained were similar to quantities reported by others (approximately 9:1 or 10:1 fulvic to humic acids; Malcolm, 1991). The isolation procedures employed in this research and by the IHSS were considered to be comparable.

Results of elemental analyses and molecular weight determinations are shown in Table 4.3. The ash content was not determined due to limited sample quantities; however the sum of the elemental analyses were generally within 5 % of 100 %, indicating that the contribution of inorganic species would likely be minimal in most cases. Average molecular weights determined for the XAD-8 isolated fulvics compare well with those provided for the IHSS material and are larger than those for the XAD-4 fulvics. Elemental analyses performed on the river water NOM isolates showed them to be generally similar to the IHSS material except that the local isolates have approximately six times the sulfur content and only 85 to 90 % of the carbon content. This relatively lower carbon content is a result of higher contributions from other elements. The nitrogen content of these samples is similar for the XAD-8 isolates but that of the XAD-4 isolates is approximately 1.5 times that of the material isolated on XAD-8. For both the lakewater and river water isolates, the XAD-4 isolates contain approximately 1.5 times the amount of nitrogen as do the XAD-8 isolates. The nitrogen content is also a major distinguishing feature between the river and lakewater NOM, the lakewater containing 4 to 5 times the levels as the river water isolates. As for the sulfur content, all four of the local isolates contain 3 to 8 times the sulfur of the IHSS material. XAD-4 isolates contain less than XAD-8 isolates (22 % less for river NOM and 62 % less for lakewater NOM).

The hydrophilic bases isolated on the AG MP-50 ion exchange resin displayed different characteristics from those of the hydrophobic and acidic components isolated on the XAD resins. Lower carbon and oxygen contents were compensated by higher nitrogen and sulfur levels. The higher nitrogen content (18.65 %) was not surprising since amino compounds would be expected to be isolated under the conditions employed. The higher sulfur content may have been from mercapto compounds, but was more likely due to sulfate not removed from the isolated NOM during the clean-up procedures as discussed in relation to the IR data presented later in this section.

Table 4.3 Elemental Analysis and Average Molecular Weight of Fulvic Acids and Hydrophilic Bases

NOM Fraction and Source	Elemental Analysis (%)					Mean Molecular Weight (g/mol)
	C	H	N	O	S	
XAD-8 NOM						
IHSS Suwannee River	53.60	4.25	0.70	40.90	0.55	1110
N. Saskatchewan River	47.05	4.66	0.72	41.97	3.91	900
Driedmeat Lake	42.79	4.55	3.72	40.26	4.38	1045
XAD-4 NOM						
North Saskatchewan River	43.37	4.67	1.07	44.55	3.04	467
Driedmeat Lake	45.34	4.88	4.24	41.64	1.67	627
AG MP-50 NOM						
North Saskatchewan River	16.66	6.44	17.65	25.42	23.35	NA

NA = not available
XAD-8, XAD-4 = Fulvic Acids; AG MP-50 = Hydrophilic Bases.

Average molecular weights determined for each isolate indicate that as expected, the XAD-8 fulvic acids are larger molecules than the XAD-4 isolates. XAD-4 isolates were measured at 467 daltons for river water fulvics and 627 daltons for lakewater fulvics, whereas values of 900 and 1045 daltons were obtained for the XAD-8 river and lakewater fulvic acids, respectively. Molecular weights of the NOM isolated with XAD-8 resin compare well with those determined for the IHSS material (1110 daltons, MacCarthy, 1992).

UV absorbance data were obtained at 254 nm and 270 nm for comparison with literature values and are shown in Table 4.4. UV/VIS spectra did not provide much additional information and are contained in Appendix III. The data shown in Table 4.4 indicate the degree of unsaturation of each of the fractions and may be useful in predicting the extent of reaction with ozone by molecular mechanisms. The measurements made at 270 nm were for comparison with results reported by Xiong *et al.* (1992) and Paillard *et al.* (1989) in which fulvic acids isolated on XAD-8 resin were ozonated. The NOM fractions isolated in this study were similar to those reported by Xiong *et al.* The XAD-8 fractions had higher UV absorbances than did the XAD-4 fractions (0.0281 to 0.0320 vs 0.0210 absorbance units/cm per mg/L NVDOC) which indicates that there are differences in chemical characteristics between the materials isolated by the two resins. However values for the XAD-8 isolates compare well with those of Xiong *et al.* (1992) and, considering possible measurement errors, all values may be within the range of 0.0215 to 0.0358 reported by them for fulvics isolated solely on XAD-8 resin in France. These data corroborated the IR data and also agreed with the general trend of colour intensity for each of the fractions. The more highly coloured fractions were associated with higher UV absorbance values, indicating greater degrees of unsaturation.

IR spectra of the river water fulvic acids (NSR4 and NSR8) were very similar to each other and are consistent with published data for similar substances (Aiken *et al.*, 1985). They are shown in Appendix III. These spectra contain absorbances typical of

Table 4.4 UV Absorbance Data*

NOM Fraction	Resin Used	UV_{254} Abs.	UV_{270} Abs.
Fulvic Acids (20 mg/L NVDOC)			
IHSS Suwannee River	XAD-8	0.031	0.032
Driedmeat Lake	XAD-8	0.030	0.028
North Saskatchewan River	XAD-8	0.032	0.028
North Saskatchewan River	XAD-4†	0.027	0.021
Fulvic Acids (5 mg/L NVDOC)			
Driedmeat Lake	XAD-8	0.030	0.025
North Saskatchewan River	XAD-8	0.032	0.026
Driedmeat Lake	XAD-4	0.023	0.018
North Saskatchewan River	XAD-4	0.027	0.022
Hydrophilic Neutrals (5 mg/L NVDOC)			
North Saskatchewan River	AG MP-50††	0.007	0.006

* UV absorbance units /cm/mg/L NVDOC, pH 6, all values measured in house.
† XAD-4 resin was placed after XAD-8 resin.
†† AG MP-50 resin was placed after XAD-4 resin.

carboxyl OH (3000 - 3500 cm^{-1}) and CO stretches. Peaks at 1200 and 1720 cm^{-1} are indicative of ionic carboxyl groups, possibly formates or acetates whereas peaks at 1600 and 1200 cm^{-1} are aliphatic ketones (1300 cm^{-1} for aromatic) although some contribution may originate from quinone type moieties. The peak at 1400 cm^{-1} is larger in NSR4 than NSR8, and together with the 1600 cm^{-1} peak (which is small) may indicate a higher carboxyl content. Also, NSR4 appears to have more aliphatic content than NSR-8 (peaks at 2900 cm^{-1}).

The lakewater fulvic acids (DML4 and DML8) were more distinct. The 1400 cm^{-1} peak for the lakewater fulvics was much larger than for river water fulvics, as was the 1600 cm^{-1} peak (well defined in DML4 only) which indicate higher carboxyl content for the lakewater fulvics. A peak at 1700 cm^{-1} was also present (higher in DML4), representing carboxylic acids in ionic form, possibly as formates or acetates.

XAD-4 fractions were more aliphatic in nature and showed a greater degree of carboxyl content than their XAD-8 counterparts. No humic acids were isolated on the XAD-4 resin, only fulvic acids, also indicating the relatively more polar and hydrophilic nature of the XAD-4 isolated NOM. Spectra of the AG MP-50 isolates were quite different from those of the XAD isolates. They contained very little aromatic character by comparison but did have some carboxyl content. A very large absorbance at 1100 cm^{-1} indicated possible sulfate contamination, however this contamination would not be expected to affect ozonation reaction mechanisms with the isolated NOM.

^{13}C Nuclear magnetic resonance (NMR) spectra for selected fulvic acid fractions are shown in Appendix III. This technique requires long periods of signal averaging, two to ten hours or more, to obtain well resolved spectra (Hayes *et al.*, 1989). In the present research, two hour analyses could be accomodated. The resulting spectra illustrate fulvic acid characteristics which corroborate those obtained by FT-IR and UV analyses, and are qualitatively similar to those provided by the IHSS for Ohio River fulvic acid in their relative peak intensities (Appendix III). The large resonance between 20 and 45 ppm chemical shift (relative to trimethylsilane) originates from unsubstituted aliphatic and methyene carbons, and that from 65 to 85 ppm is carbon in hydroxylated compounds, ring carbons of polysaccharides or aliphatic ether carbons (Malcolm, 1990a). The peak at 162 to 190 ppm represents carbonyl carbons including esters and amides, and that at 125 to 130 ppm is from aromatic carbons (120 to 140 ppm being unsubstituted and alkyl substituted aromatic carbon, 118 to 120 ppm being aromatic carbon *ortho* to oxygen-substituted aromatic carbon). Because of their expense and because this preliminary data corroborated those obtained from other analyses, these tests were not continued.

The differences in NOM fraction characteristics are compared with differences in DBPs formed on ozonation in later chapters of this thesis.

4.2 Summary

The NOM isolation procedure performed in this research was consistent with that employed by others (Malcolm, 1991). Chromatographic effects were qualitatively similar, although the resin capacity greatly exceeded expectations. Yields of NOM fractions were in agreement with calculations made based on NVDOC measurements and were similar to those obtained by others with similar NVDOC. The relative characteristics and amounts of humic and fulvic acid obtained agreed with that published in the literature. Similar comparisons were made during isolation of the hydrophilic base fraction using the procedure described by Leenheer (1981).

Both UV absorbance and NVDOC measurements were useful in monitoring the adsorption process. The methods were complementary in that NVDOC measurements sometimes detected non-humic interferences (methanol), while UV absorbance measurements were specific for the coloured, humic material and were a better indicator of the adsorption of that material.

Chemical and spectral characteristics of the fulvic acids isolated on XAD-8 resin were similar to those for a corresponding "reference" grade material available from the

IHSS, but some differences such as nitrogen content were attributed to source water type differences (eutrophic lake *vs* river). Differences between XAD-8 and XAD-4 fulvic acid fractions were in their aromatic/aliphatic contents, carboxyl content and average molecular weight. The XAD-4 isolates were more aliphatic, had greater carboxyl content, and were of lower average molecular weight than were the XAD-8 isolates. UV absorbance differences for the two fractions could not be solely ascribed to differences in molecular weight.

Characteristics of the hydrophilic bases were quite different from those of the fulvic acids, most notably in their highly aliphatic character, lack of colour and high nitrogen content. This was not surprising as the procedure was expected to isolate organic amines.

CHAPTER 5

ORGANIC DBPS RESULTING FROM THE OZONATION OF ISOLATED NOM FRACTIONS AND NATURAL WATER MATRICES

Presented in this chapter are the results of ozonation experiments performed both with fractionated NOM and NOM in its natural water matrix. The NOM fractions were obtained from two water sources, a river (nominally 1.5 mg/L NVDOC) and a lake (nominally 15 mg/L NVDOC). Ozonation of the isolated fulvic acid fraction was performed at two different organic concentrations (20 and 5 mg/L NVDOC), the higher concentration in initial experiments to facilitate DBP measurement. Two raw waters from which the fulvic acid fractions were obtained were also ozonated.

Full 2^3 factorial experiments with three midpoints were performed to investigate the effects of pH (6, 8), alkalinity (0, 200 mg/L as $CaCO_3$) and ozone dosage (1:1 and 3:1 applied ozone:NVDOC mass ratio) on UV absorbance reduction and the formation of the organic DBPs listed in Table 5.1. The ranges for pH and alkalinity were chosen to encompass or slightly exceed those expected in raw waters which are used as drinking water sources. Ozone dosages were selected to reflect current drinking water treatment practice (1:1 ozone:NVDOC mass ratio) and to investigate a very high dosage (3:1), to observe any major differences in UV reduction or DBP production. The ozonation experiments were performed in semi-batch mode where gaseous ozone was generated from oxygen and then bubbled into solutions of NOM. This nomenclature is consistent with that of other North American researchers, for example Glaze *et al.* (1992). Ozonation times were adjusted to attain either a 1:1 or 3:1 mass ratio of applied ozone dose to NVDOC. All experiments were performed at room temperature (nominally 20 °C).

For the following discussion, the variance of the replicated midpoints in each experiment was calculated and used to aid in the identification of significant parameter effects as described in Chapter 3. The resulting confidence intervals are tabulated in

Table 5.1 Organic Ozonation Compounds

Class	Compound
Aldehydes	Formaldehyde
	Acetaldehyde
	Glyoxal
	Methyl glyoxal
Oxoacids	Pyruvic acid
	Oxalacetic acid
	Glyoxalic acid
	Ketomalonic acid
Carboxylic Acids	Formic acid
	Acetic acid
	Propanoic acid
	Benzoic Acid

Appendix IV, rather than complicating the text by including this statistical data in the discussion of each comparison. In general, parameter effect differences of more than approximately 10 % were statistically significant at the 90 % or 95 % confidence level. Therefore, a 10 % difference criterion may be used by the reader as a guide in identifying significant effects.

In addition to quantifying the production of DBPs, colour reduction resulting from the application of ozone (measured as UV absorbance at 270 nm) was determined. Attempts were also made to correlate DBP production with UV absorbance reduction.

One advantage of using a factorial type of experimental design is that it allows the effects of interactions between individual parameters to be evaluated. Since experimental parameters do not necessarily affect observed results independently, the factorial design was used to estimate the extent of the interaction or synergistic effects of each of the parameters investigated.

5.1 Ozonation of Isolated Fulvic Acids at 20 mg/L NVDOC

Experiments were conducted at high organic concentrations (20 mg/L NVDOC) using three NOM fractions which were isolated from locally available sources (Alberta, Canada), and one fulvic acid originating from the Suwannee River (Southeastern USA) which was obtained in "reference" grade purity from the International Humic Substances Society (IHSS). Local fulvic acid fractions were isolated from Driedmeat Lake water using XAD-8 resin (designated as DML8) or from the North Saskatchewan River water using XAD-8 or XAD-4 resin (NSR8 or NSR4, respectively). These fractions allowed source differences as well as individual NOM fractions to be investigated. The NVDOC concentration of 20 mg C/L, which is higher than would generally be encountered in drinking water treatment, was chosen to facilitate DBP detection.

5.1.1 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance

The effects of various ozone dosages and water quality parameters (pH, alkalinity) on reduction of UV absorbance, which is related to colour reduction, were studied as a subset of the factorial to investigate DBP production. UV measurements were conducted at 270 nm for comparison with data reported by Xiong *et al.* (1992).

The mean effects of pH, alkalinity and ozone dosage on the ability of ozone and/or associated free radical species to react with UV absorbing moieties (sites of aromaticity and unsaturation) are illustrated in Figure 5.1. Shown are the UV absorbance reductions relative to their initial values prior to ozonation.

Each parameter was observed to exert a significant effect on UV reduction under the experimental conditions employed. Greater UV reductions were associated with high pH, high alkalinity and higher ozone dosages. UV absorbance reductions observed at the higher pH and alkalinity were two to six times greater than absorbance reductions observed at lower pH and alkalinity set points.

The greater UV absorbance reductions observed when the alkalinity was high can be explained by the following arguments, consistent with the literature. Molecular ozone is known to react specifically at sites of unsaturation in molecules (UV absorbing sites). High alkalinity promotes molecular ozone reaction mechanisms, especially during initial reaction periods, and can also reduce the subsequent radical reaction mechanisms occurring at longer reaction times (Xiong *et al.*, 1992). Alkalinity scavenges free radical species associated with ozone and enables prolonged molecular ozone life, permitting the more selective molecular reactions which result in UV absorbance reductions to occur. Conditions which favour the molecular reactions (low pH, high alkalinity) have been specifically recommended for UV reduction in water treatment applications.

At first glance, the data pertaining to pH effects seem to contradict what is known about ozonation of fulvic acids. Greater UV reductions were realized at pH 8 than at pH 6 (Figure 5.1), whereas higher reductions are normally expected at pH 6. The following

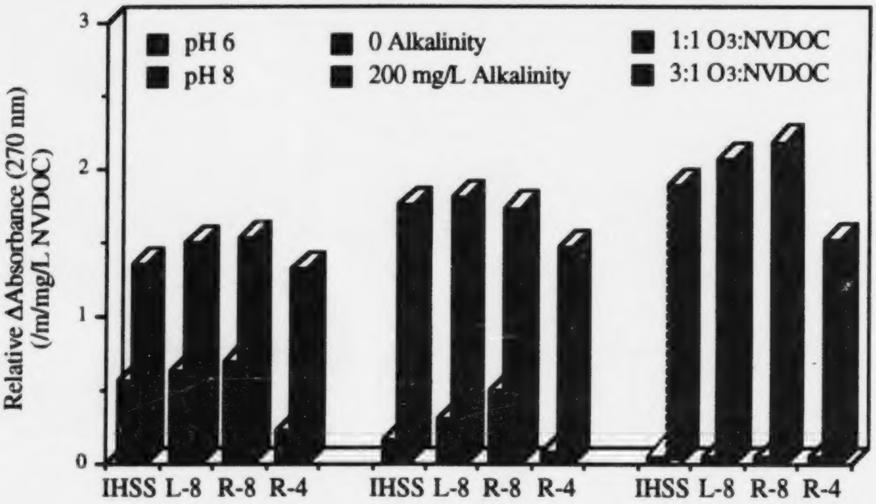


Figure 5.1 Effect of pH, Alkalinity and Ozone Dose on Reduction of UV Absorbance of NOM Fractions. (IHSS = reference material, L = lakewater source, R = river water source, 8 or 4 = XAD-8 or XAD-4, 270 nm; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

explanation is offered, based on the relative kinetics of the molecular and free radical reactions. The free radical pathway is very fast ($k_{OH\cdot}$ of the order of 10^7 to 10^9 M^{-1} sec^{-1}) compared with the molecular one (k_{O_3} of the order of 10^2 to 10^3 M^{-1} sec^{-1}) (Xiong and Legube, 1991; Staehelin and Hoigné, 1985). As such, because reaction times were relatively short and the ozone was constantly added to the test solutions, the higher UV reduction observed at pH 8 relative to that at pH 6 may be the result of the difference in the kinetics of the two reaction mechanisms. Observed higher ozone residuals for test solutions at pH 6 (Appendix IV) indicate that a lesser amount of ozone reacted at this pH, supporting this theory.

The radical scavenging ability of NOM may also play a small part in the observed pH effect. At high pH the hydroxide ion increases ozone decomposition causing reactions by rapid free radical mechanisms to become more predominant. Although the reaction of ozone with UV absorbing moieties is well-defined for molecular ozone, reaction by radical mechanisms also occurs. However, one might expect the extent of UV reduction to be lower under strictly free radical as opposed to strictly molecular conditions for a given ozone dose since free radicals are less specific for UV absorbing loci than are molecular reactions. In the same way that alkalinity reacts with free radicals, thereby enhancing the molecular reaction pathway, fulvic acids themselves also react with radicals induced at high pH and enhance the molecular reaction pathway (Staehelin and Hoigné, 1985). Kelly (in Glaze *et al.*, 1992) reported that solutions of 2 mg/L DOC can contain as much as 4 times the hydroxyl radical scavenging reactivity as 200 mg/L $CaCO_3$. When fulvic acids react with ozone-associated radicals they form intermediates which may or may not promote further free radical reactions. Extremely high concentrations of fulvic acid can override alkalinity effects because at longer reaction times or higher ozone dosages, the free radical promoting aspects of fulvic acids on ozonation are evident (Xiong *et al.*, 1992). Therefore, it may be that at pH 8 the hydroxide ion concentration may be too low to cause the radical reaction mechanism to entirely predominate over the molecular mechanism at the concentration of fulvic acids employed. Both reaction mechanisms may therefore contribute to the observed effect of UV reduction.

Ozone dosage was the parameter which displayed the greatest effect on UV reduction (Figure 5.1). At 20 mg/L NVDOC, an increase in applied ozone dose from 1:1 to 3:1 ozone:NVDOC produced a greater than 90 % reduction in UV absorbance. The ozonation conditions of this study were such that a 1:1 or 3:1 ozone:NVDOC mass ratio was achieved following either a 30 or 90 second application of ozone. One can compare the results of this research with those of Xiong *et al.* (1992) and Xiong and Legube (1991) in which ozone was added at one time to a static reactor. They demonstrated that at low pH and for short reaction times molecular reactions predominated. When the reaction time was increased, evidence of both molecular and radical mechanisms was observed. At high pH, radical reaction mechanisms were observed throughout the reaction time. In the present study, the lower ozonation time may be compared to the short reaction times of Xiong *et al.* (1992) or to the conditions employed by Xiong and Legube (1991) for which radical reactions did not significantly participate. Conversely, the greatly increased change in UV absorbance observed following an increase in the applied ozone dose from 1:1 to 3:1 ozone:NVDOC may be due to an increased participation of the fulvic acids in promoting radical formation, thereby compounding the observed effect. At an NVDOC concentration of 20 mg C/L then, the transition of fulvic acids from primarily scavengers to promoters in radical reactions may occur between a 1:1 and 3:1 ozone:NVDOC mass ratio of applied ozone dose.

These results can also be compared with those of Staehelin and Hoigné (1985) in which fulvic acids ozonated at low ozone dosages acted as radical scavengers while at higher ozone dosages they behaved as promoters of radical reactions. In the present research, then, one would expect the reduction in UV absorbance to be more than proportional to the increase in dose. This effect was observed, as shown in Figure 5.1, where a three-fold increase in dose produced at least a ten-fold reduction in UV absorbance.

In a separate set of experiments performed at lower organics concentrations (5 mg/L NVDOC) the increase in UV reduction for similar increases in ozone:NVDOC ratios was only approximately 30 to 50 % (Section 5.2). Earlier research by others reported little concentration dependence but utilized extremely high fulvic acid concentrations (1 to 5 g/L fulvic acids, Anderson *et al.*, 1986a). At a constant ozone:NVDOC ratio, the ratios of ozone:alkalinity and ozone:hydroxide ion concentration will be dependent on NVDOC concentration. Therefore, the NVDOC concentration appears to play an important and perhaps complex role in the reduction of UV absorbance by ozone.

Absolute UV reductions were generally slightly greater for NOM fractions isolated on XAD-8 resin than from those isolated on XAD-4, regardless of the ozonation parameter under investigation (Figure 5.1). At pH 6, where molecular ozone mechanisms are important, reduction of XAD-4 fulvic acid UV absorbance was small (2.5 abs/cm/mg/L NVDOC) relative to those of the XAD-8 fractions (6 to 7.5 abs/cm/mg/L NVDOC), likely because they contain fewer sites of unsaturation and, therefore, fewer sites for reaction with molecular ozone. At pH 8, where the less selective radical mechanisms operate, UV reductions of 13 to 16 abs/cm/mg/L NVDOC were approximately comparable among all NOM fractions tested. However, relative changes in the UV absorbances were greater for the XAD-4 resin fractions. For example, when considering ozonation of XAD-4 isolated river water NOM, increasing the alkalinity from 0 to 200 mg/L as $CaCO_3$ increased the reduction in UV absorbance by 14 times. In contrast, ozonation of the river water NOM isolated on XAD-8 under similar alkalinity conditions increased the UV absorbance reduction by only a factor of 2.4.

In summary, UV absorbance reductions of up to 20 abs/cm/mg/L NVDOC which correlated with reduction in colour, occurred at pH 8, high alkalinity (200 mg/L as $CaCO_3$) and at the higher applied ozone dose (3:1 ozone:NVDOC). For the concentration of

NVDOC used and the ozonation parameter values studied, it was apparent that the fulvic acids likely reacted both as radical scavengers and promoters, and that the transition between the two states might lie between the ozone dosages of 1:1 and 3:1 ozone:NVDOC.

5.1.2 Aldehyde, Oxoacid and Carboxylic Acid Production

The organic DBPs of interest in this research are listed in Table 5.1 and include three classes of compounds: aldehydes, oxoacids and carboxylic acids. Ozone has been shown to produce all of these compounds in natural waters (Glaze, 1986; Xie and Reckhow, 1992a). Some of them are of toxicological interest (aldehydes, oxoacids; Basu *et al.*, 1988)) while others contribute to distribution system water instability by providing nutrient material to support microbial regrowth (carboxylic acids, aldehydes, possibly oxoacids; Anderson *et al.*, 1990a; Xie and Reckhow, 1992a).

Full 2^3 factorial experiments with three midpoints were performed to investigate the effects of pH (6, 8), alkalinity (0, 200 mg/L as $CaCO_3$) and ozone dosage (1:1, 3:1 applied ozone:NVDOC mass ratio) on the formation of the organic DBPs listed in Table 5.1. The results are shown in Figures 5.2 to 5.5. In order to determine the mean effects of the ozonation parameters on the classes of DBPs shown, data for aldehyde, oxoacid and carboxylic acid concentrations were converted to their molar values and summed for each class of by-product. Not included in the carboxylic acids are data for the dicarboxylic acids, which are not measurable by the methods employed. Due to the factorial design of the experiment, the data allow the effects of each of the three factors to be determined separately. If enough of the individual DBP species have been chosen to accurately represent each class, the relative amounts of the various classes of by-products can be inferred from these results.

The results presented in Figures 5.2 to 5.5 show that at 20 mg/L NVDOC, aldehydes and carboxylic acids formed the majority of the by-product classes studied relative to the oxoacids. Please note the difference in scales used for the y axes. There are

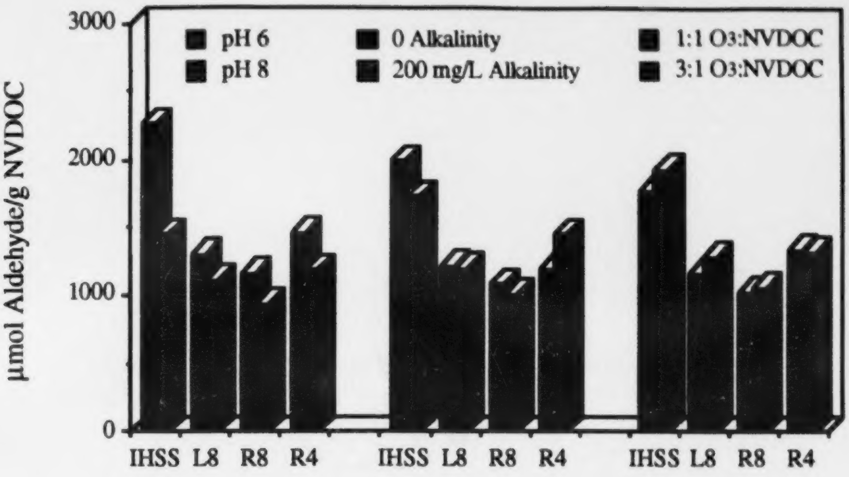


Figure 5.2 Effects of pH, Alkalinity and Ozone Dose on Formation of Aldehydes During Ozonation of NOM Fractions at 20 mg/L NVDOC (IHSS = reference material, L = lakewater source, R = river water source, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

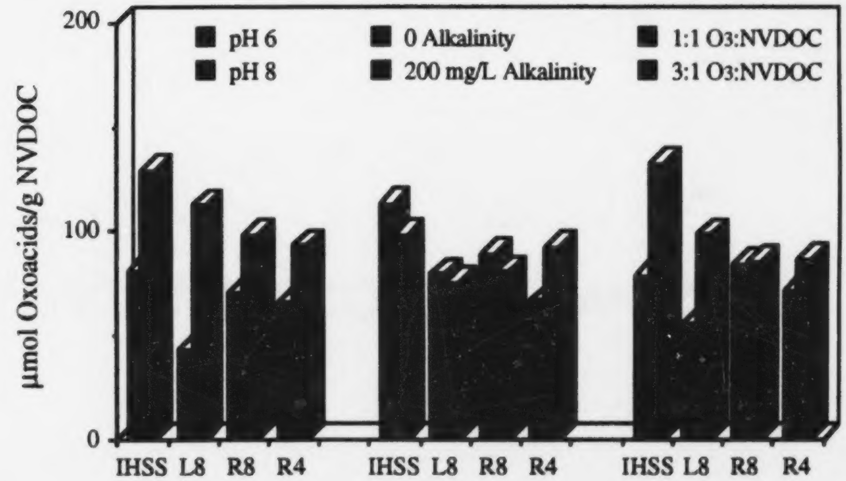


Figure 5.3 Effects of pH, Alkalinity and Ozone dose on Formation of Oxoacids During Ozonation of NOM Fractions at 20 mg/L (IHSS = reference material, L = lakewater source, R = river water source, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

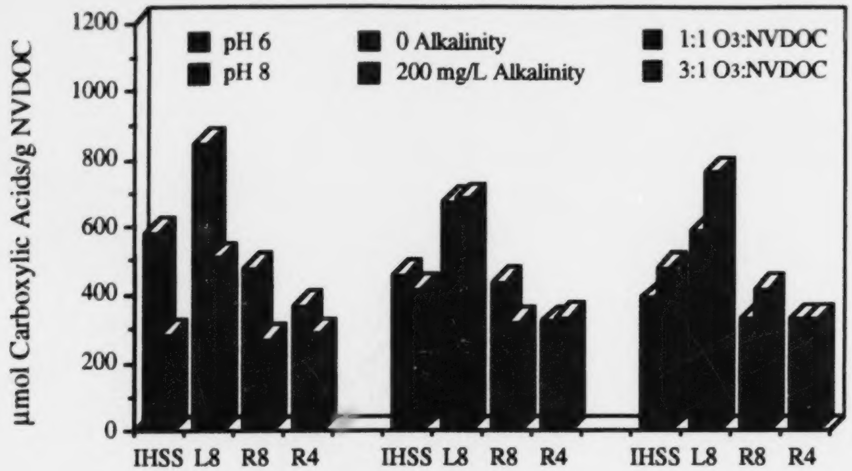


Figure 5.4 Effects of pH, Alkalinity and Ozone Dose on Formation of Carboxylic Acids During Ozonation of NOM fractions at 20 mg/L (IHSS = reference material, L = lakewater source, R = river water source, 8 or 4 = XAD-8 or XAD-4; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

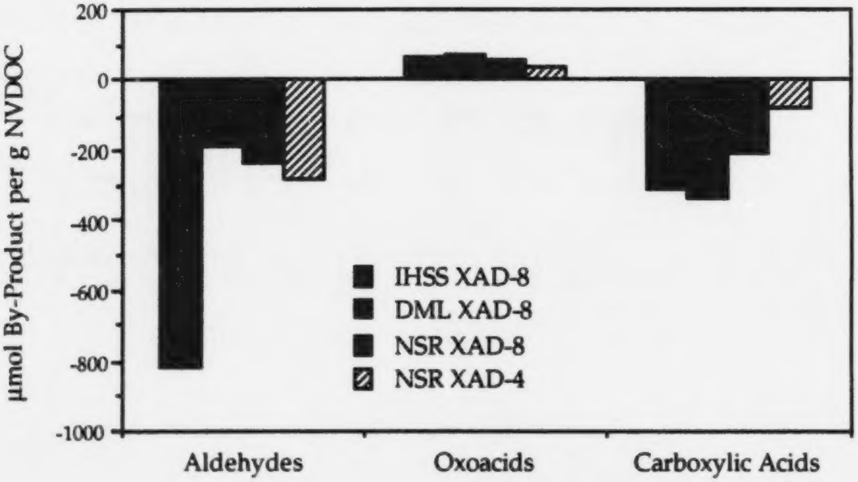


Figure 5.5 Main Effects of Increasing pH from 6 to 8 on DBP Formation for Four Different Fulvic Acids at 20 mg/L NVDOC (IHSS, DML, NSR = reference, lakewater, river water source; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

at least two possible explanations for the relative abundances of these classes of compounds. One is that portions of the fulvic acids may be progressively oxidized from aldehydes to carboxylic acids, and in the process become multiply oxidized to oxoaldehydes, oxoacids and others before being finally oxidized to simple carboxylic acids. Should this be the case, the relative abundances of the different classes may indicate the relative activation energies for formation of oxoacids, aldehydes and carboxylic acids from fulvic acid ozonation. Another possible explanation for the relative abundances is that each class results from different precursors, *i.e.* different portions of the fulvic acid molecules, and that different amounts of the precursor materials were available for oxidation.

pH was the parameter which influenced by-product formation to the greatest extent. The effect of pH on aldehyde and carboxylic acid formation (Figures 5.2 and 5.4) was different from that on oxoacid formation (Figure 5.3). These observations are also illustrated in Figure 5.5, for which the mean DBP yields obtained at pH 8 have been subtracted from those at pH 6, the result being deemed the "main effect" of a pH change from 6 to 8 (Appendix IV). The data presented in this way clearly show that the formation of aldehydes and carboxylic acids was favoured at low pH (the yields decrease on increasing from pH 6 to 8), while that of oxoacids proceeded with greater yield at pH 8. This effect can be explained by making reference to the mechanisms of molecular ozone reaction, also known as ozonolysis. At pH 6, this molecular reaction occurs at sites of unsaturation to directly produce aldehydes which can be readily oxidized to form carboxylic acids (Glaze, 1986). At pH 8, radical reaction mechanisms, rather than ozonolysis, become more dominant. (Examples of these reactions are given in Chapter 1.) For oxoacids, sequential reactions may occur involving both a molecular and radical step. The requirement for two reactions would explain why concentrations of these DBPs were less than those of the aldehydes or carboxylic acids. As well, it may be that the oxoacids as a species participate in radical promoting reactions, as suggested by Xiong *et al.* (1992) and

Caprio *et al.* (1987) for glyoxalic acid, and therefore are intermediates rather than end products of ozonation.

Alkalinity had a much smaller effect on DBP production than did pH. In general, higher alkalinity decreased DBP formation for all three classes of by-product by up to 15 %, 12 %, and 30 %, for aldehydes, oxoacids and carboxylic acids respectively. A few instances of increased production at higher alkalinity were noted, especially for the XAD-4 isolates. The variability in alkalinity effects may be attributed to the experimental conditions which, for some fulvic acids were such that they represented intermediate states between causing fulvic acids to be scavengers or promoters of radical reactions. Therefore, in some cases the alkalinity would suppress radical formation and in others the promoting aspect of the fulvic acid would be enough to overcome the inhibitory effects of the alkalinity with regard to DBP production.

Increasing the applied ozone dosage from 1:1 to 3:1 mg ozone:mg NVDOC resulted in higher yields of all by-products. The effect was less pronounced for the formation of aldehydes and carboxylic acids (Figures 5.2 and 5.4) than for oxoacids (Figure 5.3) and was, in general, smaller for river water NOM than for lakewater NOM. It may be that the molecular reaction is facile and that sites of unsaturation react quickly with molecular ozone to form aldehydes and carboxylic acids even at lower ozone doses. As has previously been stated, these sites react preferentially with molecular ozone. The greater ozone dosage effects observed for oxoacids formation may be due to a possible radical promoting ability of this class of compounds, and may also be related to the large dose effects observed for UV absorbance reduction on ozonation of fulvic acids.

On further examination of Figures 5.2 to 5.4 it is apparent that the yields of aldehydes and carboxylic acids were most strongly influenced by the source of the fulvic acids being ozonated. Locally obtained lakewater NOM produced similar amounts of aldehydes and oxoacids to those produced by river water isolates but yielded 1.5 to 2 times the amount of carboxylic acids. Oxoacid and carboxylic acid data for IHSS NOM were similar to those obtained for locally isolated river water NOM; aldehyde concentrations were higher for the IHSS NOM. These results have implications with regard to water treatment methods and distribution system stability. Carboxylic acids are important in microbial metabolism and are not readily removed by traditional physical/chemical treatment methods. Biological treatment, however, has been shown to reduce concentrations of biodegradable material, which most certainly include carboxylic acids.

The river water NOM isolated on XAD-4 resin produced similar amounts of DBPs to XAD-8 isolates, therefore fraction type was not a factor which influenced DBP production in these experiments. However, the lower molecular weight and higher carboxyl content of the DBP precursors isolated on XAD-4 resin may indicate that their removal during treatment could be different than those isolated on XAD-8.

DBP yields from the IHSS reference material were comparable to those from the river water NOM, except that the IHSS material produced higher concentrations of aldehydes. This may be due to differences in source water characteristics.

All these data underscore the importance of the nature of the raw water NOM in the formation of ozonation by-products. Therefore, the global application of ozonated DBP data obtained from a few locations may be difficult or impossible. To a lesser extent, seasonal water quality changes occurring in some source waters may have significant impacts on ozonation DBP production.

In summary, for the concentration of NVDOC used and the ozonation parameter values studied, it was apparent that the fulvic acids may have reacted both as radical scavengers and promoters, and that the transition between the two states might lie between the two ozone:NVDOC dosage ratios investigated. With regard to organic by-products of ozonation, pH was the parameter having the greatest influence on DBP yields. The influence of pH on the formation of oxoacids was different than for aldehydes and carboxylic acids, possibly because of this participation in different reaction mechanisms (molecular *vs* radical). Also, DBP formation characteristics were somewhat site specific in that lakewater ozonation produced higher levels of carboxylic acids whereas IHSS river water NOM ozonation produced greater quantities of aldehydes.

5.1.3 Correlations Between UV Absorbance and DBP Formation

At lower NVDOC concentrations (5 mg C/L), a correlation has been demonstrated between oxoacid production and UV absorbance reduction (Section 5.2.3). Although this reduction was specific to each type of NOM, the correlations were good ($r^2 > 0.95$). In experiments utilizing high NVDOC concentrations (20 mg C/L), the correlation was much weaker ($r^2 < 0.42$), possibly because of the greater complexity of reactions occurring at these high concentrations. The correlation observed at the lower NVDOC concentration was significant at a 1% level whereas the correlation at 20 mg/L NVDOC was not significant at even the 5 % level.

5.1.4 Ozonation Parameter Interactions

Since experimental parameters do not necessarily affect observed results independently, the factorial design can be used to determine the extent of interaction or synergistic effects of each of the parameters investigated. In addition, optimal conditions for DBP formation can be inferred.

Illustrated in Figures 5.6 to 5.9 are the interactive effects of pH and alkalinity on aldehyde and oxoacid formation for NOM ozonated at two ozone dosages. Shown are data for the ozonation of river water NOM (20 mg/L NVDOC) which was isolated on XAD-4 resin. The response surfaces are of experimentally determined DBP concentrations (µmol DBP/g NVDOC, shown in bold) plotted at the conditions of pH (as hydrogen ion concentration [H^+]) and alkalinity (mg/L $CaCO_3$) under which they were determined. Also shown are contours of equal DBP response, manually drawn to give a visual appreciation of the effects. The midpoint values are shown in parentheses because they were obtained at an intermediate ozone dose (2:1 ozone:NVDOC mass ratio). A more detailed examination

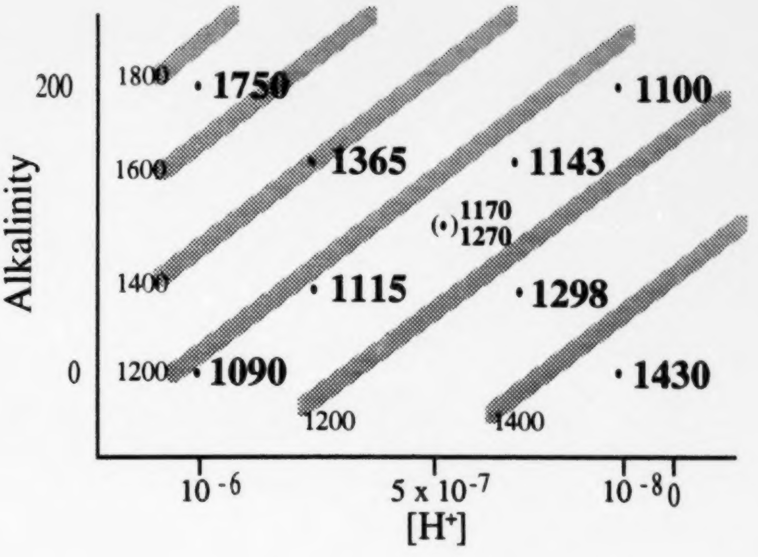


Figure 5.6 Response Surface for Interaction of Alkalinity and pH on Aldehydes Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin (1:1 ozone:NVDOC mass ratio; values in bold are experimental aldehyde data as µmol/g NVDOC)

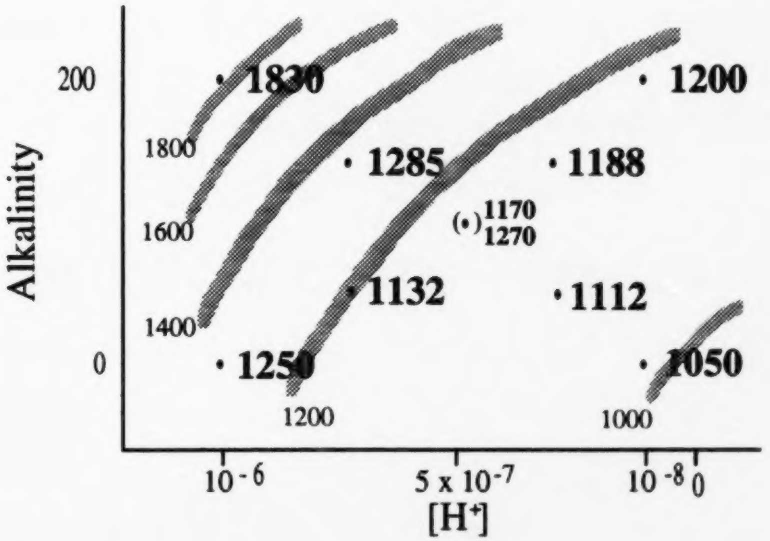


Figure 5.7 Response Surface for Interaction of Alkalinity and pH on Aldehydes Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin (3:1 ozone:NVDOC mass ratio; values in bold are experimental aldehyde data as µmol/g NVDOC).

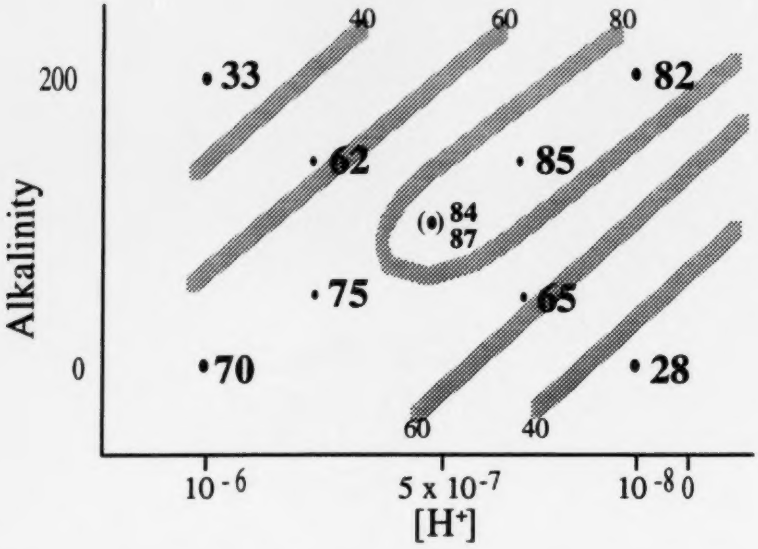


Figure 5.8 Response Surface for Interaction of Alkalinity and pH on Oxoacids Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin (1:1 ozone:NVDOC mass ratio; values in bold are experimental oxoacid data as µmol/g NVDOC)

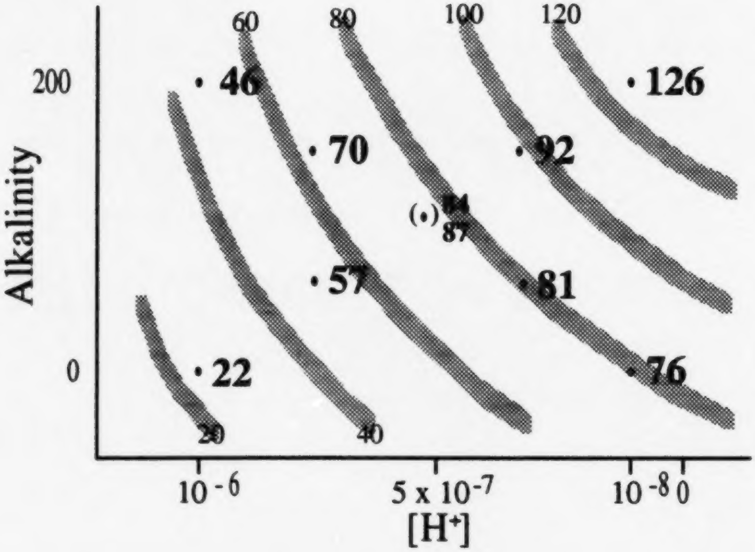


Figure 5.9 Response Surface for Interaction of Alkalinity and pH on Oxoacids Formation During Ozonation of River Water NOM Isolated on XAD-4 Resin (3:1 ozone:NVDOC mass ratio; values in bold are experimental oxoacid data as µmol/g NVDOC)

of these data for model formulation purposes was not attempted due to the limited number of data points.

The effects of pH and alkalinity on aldehyde formation at the lower ozone dose of 1:1 ozone:NVDOC mass ratio are shown in Figure 5.6. The quantity of aldehydes produced increased as alkalinity increased and hydrogen ion concentration $[H^+]$ decreased. A minimum aldehyde formation of approximately 1100 µmol/g NVDOC was apparent. The linearity of the contours indicates that there are few significant interactions or synergistic effects between the two variables (pH and alkalinity) in the formation of aldehydes under the range of conditions employed. However, the presence of a minimum suggests that if the response surface were extended by expanding the range of the variables, it would probably be elliptical. If a mathematical model were to be formulated which describes the system it would be non-linear, containing quadratic terms with respect to $[H+]^2$ and $[\text{alkalinity}]^2$.

At the higher ozone dose of 3:1 ozone:NVDOC (Figure 5.7), the pH-alkalinity interaction appeared to increase, indicated by curvature in the contour lines of the response surface and the variable rate of increase in their values. These data show that higher aldehyde concentrations were still produced at low pH and high alkalinity, favouring participation of a molecular ozone reaction as discussed previously. The variable change in the rate of increase of the response surface contours indicates that a pH-alkalinity interaction is evident at the higher ozone dose employed. While the elliptical character of the response surface shown in Figure 5.6 as evidenced by the minimum yield contour not evident in Figure 5.7, concentration effects (discussed in Chapter 6) may have caused a shift in the contour of minimum yield, taking it out of range of the conditions employed in these tests.

pH-alkalinity interactions for the formation of oxoacids during ozonation of XAD-4 river water fractions are illustrated in Figures 5.8 and 5.9. Maximum formation of oxoacids was observed at conditions of high pH and alkalinity. Contours lines shown in

Figure 5.8, which are generally parallel indicate that there are few pH-alkalinity interactions at the lower ozone dose similar to the results described for aldehydes formation (Figure 5.6). Visualization of the effects of this proposed elliptical response surface are limited however by the number of data points.

This trend was exaggerated at higher ozone dosage (3:1 ozone:NVDOC) as shown in Figure 5.9. Oxoacid formation was greatly favoured at high pH and alkalinity, conditions where neither discrete molecular nor discrete radical reaction mechanisms are present. This data indicates that both molecular and radical reaction conditions are required for oxoacids formation. Therefore, during drinking water treatment, conditions of high pH and alkalinity would be expected to yield the maximum concentrations of oxoacids at high ozone dosages relative to NVDOC concentrations. As described earlier (Chapter 1) oxoacids have undetermined biodegradability characteristics, but that some are toxicologically significant.

In summary, the interactive effects between the ozonation variables pH and alkalinity were evaluated. Maximum aldehyde formation was observed at conditions of minimum pH and maximum alkalinity, whereas oxoacids were formed in greater quantities at conditions of high pH and alkalinity. At the lower ozone dose (1:1 ozone:NVDOC), there was an apparent minimum aldehyde formation and pH-alkalinity interactions were almost a non-effect. The interaction and synergistic effects of pH and alkalinity were most pronounced at the higher ozone dosage examined (3:1 ozone:NVDOC mass ratio).

5.2 Ozonation of Isolated Fulvic Acids at 5 mg/L NVDOC

Experiments similar to those described in Section 5.1 were repeated at a lower NVDOC concentration to determine whether the effects observed under high organic loading would be consistent at other concentrations. These studies employed fulvic acids isolated on XAD-8 and XAD-4 resins from lakewater (DML8, DML4) and river water

(NSR8, NSR4) as well as hydrophilic bases isolated from river water by ion exchange (NSRX).

Full 2^3 factorial experiments with three midpoints were conducted to investigate the effects of pH (6, 8), alkalinity (0, 200 mg/L as $CaCO_3$) and ozone dosage (1:1 and 3:1 applied ozone:NVDOC mass ratio) on UV absorbance reduction and DBP production (Table 5.1) during ozonation. Material isolated by ion exchange was only investigated for pH effects due to limited quantities of available material. Experimental parameter values were based on current drinking water treatment practice and estimated water quality parameters and were the same as at 20 mg C/L. All experiments were performed at room temperature (nominally 20 °C) and utilized a concentration of 5 mg/L as NVDOC. This concentration is more realistic for raw waters than the 20 mg C/L value used in previous experiments. The tests were performed in semi-batch mode in which solutions of fractionated NOM were ozonated with gaseous ozone. Ozonation times were adjusted to achieve either a 1:1 or 3:1 mass ratio of ozone to measured NVDOC, and a 10 minute post-ozonation time was employed prior to sampling for analysis to be consistent with contact times used in typical water treatment practice.

5.2.1 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance

The effects of the ozonation parameters (described above) on the reduction of UV absorbance of fulvic acids by ozone were included in the factorial experiments which investigated DBP production. Due to a limited supply of material, only the effect of pH was examined for the ion exchange isolates. UV data were obtained at both 254 nm and 270 nm, the latter for comparison to data recently published by Xiong *et al.* (1992); however the two sets of data were very similar therefore only the data at 254 nm are shown.

The mean effects of pH, alkalinity and ozone dosage on UV absorbance reduction are illustrated in Figure 5.10. Effects of pH and alkalinity were generally small at the

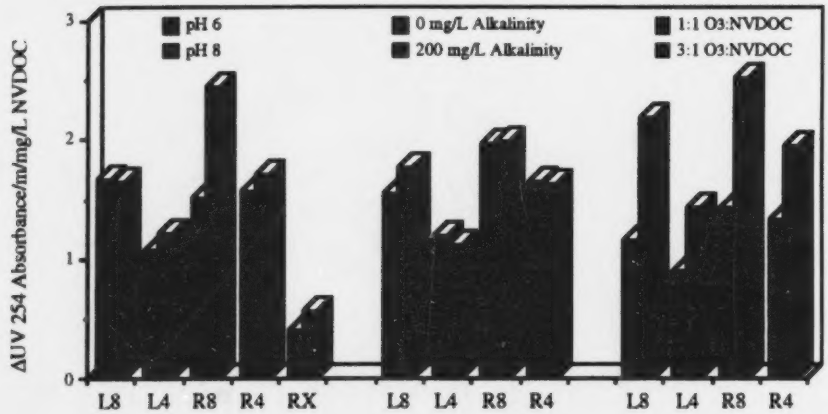


Figure 5.10 Effect of pH, Alkalinity and Ozone Dose on the Reduction of UV Absorbance (254 nm) on NOM Fractions at 5 mg/L NVDOC (L = lakewater source, R = river water source, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

NVDOC concentration studied (5 mg/L NVDOC). Small to moderate increases in UV reduction were observed when changing from pH 6 to 8 for all fractions except the lakewater NOM isolated on XAD-8. The largest effect was observed for river water NOM isolated on XAD-8. These data appeared to contradict data obtained previously at 20 mg/L NVDOC (Section 5.1) which showed strong effects for all of the parameters and NOM fractions studied. At 20 mg/L NVDOC, 2 to 6 times greater UV absorbance reductions were observed at high pH and alkalinity relative to reductions at low pH and alkalinity. It may be that the proportion of ozone consumed in reactions with inorganic water components is greater at lower NVDOC concentrations, therefore less ozone was available to react with the fulvic acids.

Ozone dose was the parameter that most affected UV reduction in experiments performed at either NVDOC concentration, although the effects were more pronounced at the higher NVDOC concentration. At 20 mg/L NVDOC, increasing the ozone dose from 1:1 to 3:1 ozone:NVDOC resulted in a greater than 90 % reduction in UV absorbance, whereas at 5 mg/L NVDOC the increase in UV reduction was approximately 30 to 50 % (Figure 5.10). Therefore, when considering ozone for removal of colour from drinking water, the NVDOC concentration effect must be taken into account.

Ozone removed more UV absorbing species from NOM fractions isolated on XAD-8 resin than from those isolated on XAD-4 or AG MP-50. Similarly, the UV absorbance of the XAD-8 fractions were more susceptible to the effects of pH and ozone dose than were other fractions. This was likely a result of the greater aliphatic nature of the XAD-4 and AG MP-50 fractions relative to the XAD-8 fractions. The XAD-4 fulvic acid and hydrophilic base fractions contain fewer sites of unsaturation and, therefore, fewer possible sites of reaction, especially for reaction with molecular ozone.

5.2.2 Aldehyde, Oxoacid and Carboxylic Acid Production

Full 2^3 factorial experiments with three midpoints were performed to investigate the effects of pH (6, 8), alkalinity (0, 200 mg/L as $CaCO_3$) and ozone dosage (1:1, 3:1 applied ozone:NVDOC mass ratio) on the formation of the organic DBPs listed in Table 5.1. In order to determine the mean effects of the ozonation parameters on the classes of DBPs, aldehyde, oxoacid and carboxylic acid concentrations were converted to their molar values and summed for each class of by-product. Not included in the carboxylic acids are data for the dicarboxylic acids, which are not measurable by the methods employed. Because of the factorial design of the experiment, the data allow the effects of each of the three factors to be determined separately. If enough of the individual species have been chosen so as to accurately represent each class, the relative amounts of the various classes of by-products can be inferred from these results.

The mean effects of pH, alkalinity and ozone dosage on organic ozonation DBP formation from fulvic acids and hydrophilic bases at 5 mg/L NVDOC are shown in Figures 5.11 to 5.13. These figures emphasize the relative DBP yields obtained in these experiments conducted at a lower NVDOC concentration. Aldehyde formation was much more dominant in these experiments than in earlier experiments conducted at 20 mg/L NVDOC (Section 5.1). The ratio of aldehydes to oxoacids was similar at either NVDOC concentration but the proportion of carboxylic acids decreased substantially at 5 mg/L NVDOC. The large yield of aldehyde tends to mask the effects observed for other DBPs and makes it appear that pH, alkalinity and ozone:NVDOC ratio have little or no effect at these lower NVDOC concentrations. However, even though concentrations of oxoacids and carboxylic acids were much lower than aldehydes concentrations, the effects of pH, alkalinity and ozone dose were qualitatively similar at both NVDOC concentrations.

The effects of the ozonation parameters, rather than the relative DBP class yields, are better illustrated in Figures 5.14 to 5.16 which display results for each of the DBP classes individually. Please note that different scales are used for each of these figures.

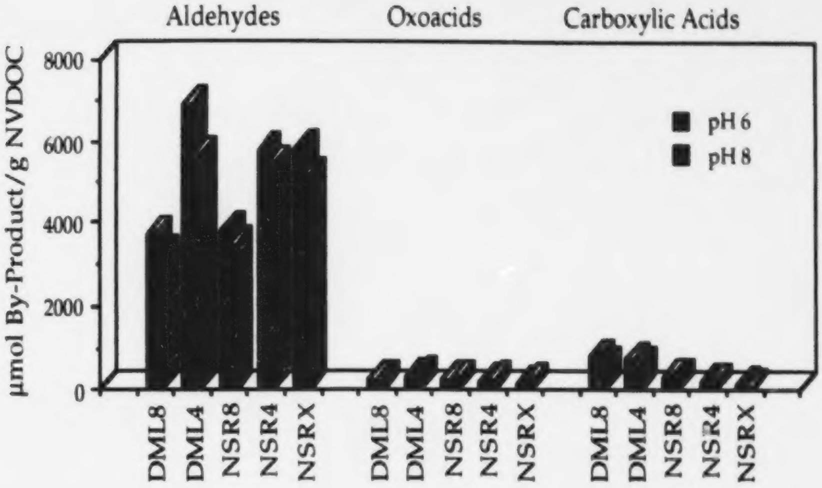


Figure 5.11 Effect of pH on the Formation of DBPs from the Ozonation of NOM Fractions at 5 mg/L NVDOC (DML = lakewater source, NSR = river water source, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

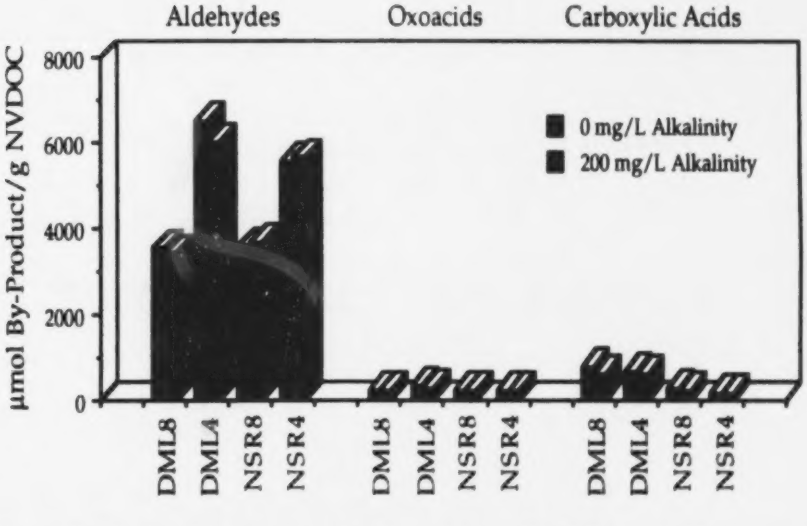


Figure 5.12 Effect of Alkalinity on the Formation of DBPs from Ozonation of NOM Fractions at 5 mg/L NVDOC (DML = lakewater source, NSR = river water source, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and dose))

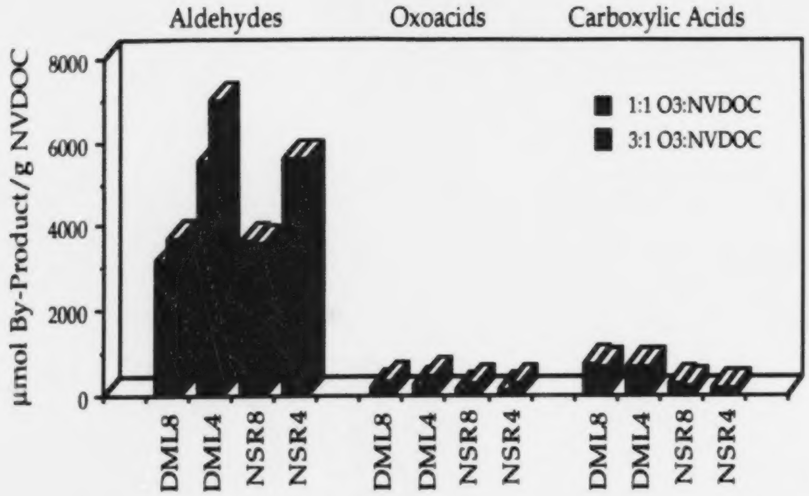


Figure 5.13 Effect of Ozone Dose on the Formation of DBPs from Ozonation of NOM Fractions at 5 mg/L NVDOC (DML = lakewater source, NSR = river water source, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

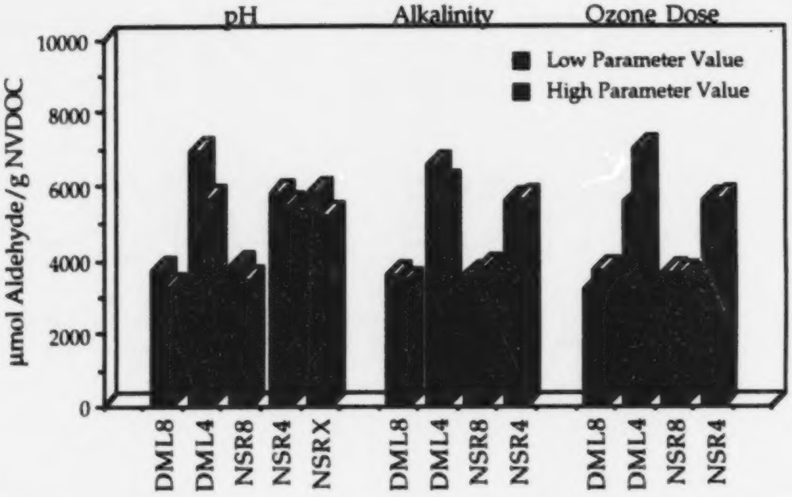


Figure 5.14 Effect of Various Parameters on the Formation of Aldehydes from the Ozonation of NOM Fractions at 5 mg/L NVDOC (DML = lakewater source, NSR = river water source, 8 = XAD-8, 4 = XAD-4, X = AG MP-50, low/high parameter values: pH 6/8, alkalinity 0/200 mg/L as $CaCO_3$, ozone dose 1:1/3:1 applied ozone:NVDOC mass ratio; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

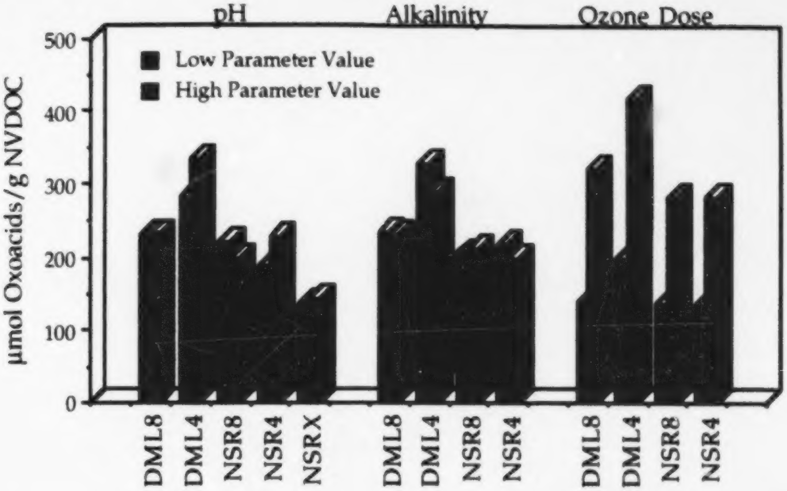


Figure 5.15 Effect of Various Parameters on the Formation of Oxoacids from the Ozonation of NOM Fractions at 5 mg/L NVDOC (DML = lakewater, NSR = river water; 8,4=XAD-8,4,; X=AG MP-50, low/high parameter values: pH 6/8, alkalinity 0/200 mg/L as $CaCO_3$, ozone dose 1:1/3:1 applied mass ratio ozone:NVDOC; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

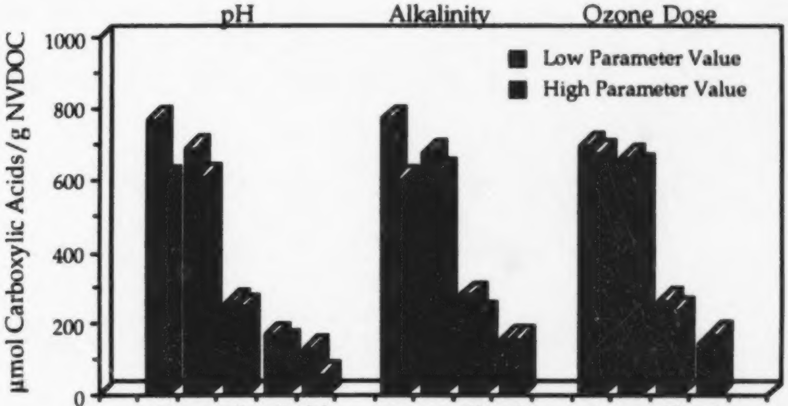


Figure 5.16 Effect of Various Parameters on the Formation of Carboxylic Acids from NOM Fraction Ozonation (5 mg/L NVDOC; DML = lakewater, NSR = river water, 8,4=XAD-8,4; X=AG MP-50; low/high parameter values: pH 6/8, alkalinity 0/200 mg/L as $CaCO_3$, ozone dose 1:1/3:1 applied mass ratio ozone:NVDOC; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

For all NOM fractions, low pH values promoted aldehyde production (Figure 5.14). Changes in alkalinity had little effect on aldehyde yields. Similarly ozone dosage had little effect on aldehyde production resulting from river water NOM ozonation but when applied to lakewater NOM higher ozone dosages resulted in an increase in aldehyde production. The lack of an observed effect with respect to ozone dose may have been due to the high ozone concentrations used (1:1 and 3:1 ozone:NVDOC mass ratios), whereas typical drinking water treatment employs ratios of 1:1 or less.

All XAD-8 fractions produced similar aldehyde yields. The yields for XAD-4 and AG MP-50 were similar to each other. In addition, NOM isolated on XAD-4 and ion exchange resins produced greater quantities of aldehydes than did fractions isolated on XAD-8 resin (Figure 5.14). For both of the two water sources, XAD-4 isolates produced up to 1.5 times the aldehydes when compared to XAD-8 isolates (Figure 5.14), but only slightly higher oxoacids (Figure 5.15). Lower carboxylic acid concentrations were observed for XAD-4 NOM than XAD-8 NOM (Figure 5.16).

Some consideration should be given to the differences in the mean molecular weights of the two types of NOM fractions when rationalizing the greater quantities of ozonation DBPs which were produced from the XAD-4 fractions than the XAD-8 fractions. Equal mass concentrations of the two types of NOM would be expected to result in higher molar concentrations of precursor material for the lower molecular weight fraction. For this molecular weight difference to be the cause of the yield discrepancies, each fulvic acid macromolecule, regardless of its size (molecular weight), would have to contain a similar number of reactive sites. For DBP formation, this may imply a surface-type phenomenon whereby only easily accessible portions of the molecule (those near an edge) react to form ozonation DBPs. This theory is possible because it is known that ozonation results in the disruption of large molecules to smaller ones (change in molecular weight) without DBP formation.

Oxoacids formation was dominated by ozone dose and pH (Figure 5.15). pH effects observed for oxoacids formation were the opposite to those observed for aldehyde and carboxylic acid production. Higher oxoacids yields generally resulted at the higher pH. Ozone dosage had a marked effect on oxoacids production regardless of the NOM source or fraction. Increasing the ozone dose from 1:1 to 3:1 ozone:NVDOC increased the oxoacids yield by a factor of two.

Carboxylic acid production was observed to be governed more by the NOM source than by NOM fraction or ozonation conditions (Figure 5.16). Lakewater NOM fractions produced similar or slightly higher amounts of aldehydes and oxoacids when compared to results using river water fractions. However, lakewater NOM produced two to three times the amount of carboxylic acids. While NOM isolated on XAD-8 resin generally produced greater quantities of carboxylic acid than did XAD-4, the differences were generally within 20 %. The lowest observed yields for carboxylic acids resulted from ozonation of the hydrophilic basic NOM which had been isolated by ion exchange.

In summary, the effects of the ozonation parameters determined at 5 mg/L NVDOC were similar to those observed at 20 mg/L NVDOC (Section 5.1.2). Therefore, similar reaction mechanisms were assumed to apply. pH was observed to affect NOM ozonation by-product formation to the greatest extent. The effect of pH on aldehyde and carboxylic acid formation was different from that observed for oxoacid formation. Formation of aldehydes and carboxylic acids were favoured at low pH values whereas greater yields of oxoacids were observed at pH 8 (for all but one fraction). Alkalinity exhibited a much smaller effect than did pH, but higher alkalinity conditions resulted in a decrease in by-product formation for all three classes of DBPs. A few instances of increased DBP production coinciding with increased alkalinity were noted, however the magnitudes of all alkalinity effects were such that they were usually within the experimental error associated with non-effects. Increasing the ozone dosage applied to the lakewater fulvic acids resulted in higher yields of aldehydes, and much higher yields of oxoacids. Slight decreases were noted for carboxylic acids. In contrast, for the river water fulvic acids, changes in ozone dosage at the levels examined had little effect on DBP yields except for the oxoacids which approximately doubled on increasing the ozone dose from 1:1 to 3:1 ozone:NVDOC, regardless of the water source or NOM fraction.

5.2.3 Correlations Between UV Absorbance and DBP Production

One of the objectives of this research was to attempt to determine quantitative relationships between NOM characteristics and the production of DBPs. UV absorbance, which is related to water colour was an obvious parameter with which to make this comparison. UV absorbance is measured in many water treatment plants. It could easily be used to model or predict DBP formation, should causal relationships exist, and has been used as a surrogate for monitoring DBP precursor material in some studies (for example, Edzwald *et al.*, 1985).

DBP production and UV reduction did not appear to correlate well at the higher NVDOC concentrations studied. In these experiments, higher UV reductions were associated with the XAD-8 fractions, whereas greater quantities of DBPs were produced by the XAD-4 fractions. Similarly, increased ozone dosages resulted in increases in UV reduction regardless of the fraction employed, but they had a variable or no effect on the production of DBPs. Therefore, the initial conclusion was that UV data could not be used to quantitatively predict DBP formation. However, some similarities were observed for the effects of ozonation on UV reduction and the formation of organic ozonation DBPs regardless of the NVDOC concentration. For example, both UV reduction and oxoacid formation proceeded to greater extents at high pH. The opposite was observed for aldehyde and carboxylic acid DBP production. In addition, while higher ozone doses resulted in only marginally increased aldehyde yields and did not affect carboxylic acid yields, the increase in oxoacids production was nearly double for a three-fold increase in ozone:NVDOC ratio.

The correlation between UV reduction and oxoacid production under the conditions of ozonation employed in these experiments is shown in Figure 5.17 for all NOM fractions except the hydrophilic bases. These components could not be included in comparisons because they had only been examined in pH experiments. Good correlations were obtained (r^2 values of greater than 0.95 at the 1 % level of significance) for all NOM fractions except one. The river water NOM isolated on XAD-8 resin showed a poor correlation (r^2 of 0.43). Similar correlations were made for aldehyde and carboxylic acid production, but the results were poor (r^2 of less than 0.4) and are not shown.

5.3 Ozonation of Natural Waters

Possible differences in the formation of organic DBPs between unfractionated NOM and the fractionated material studied up to this point were evaluated using samples of raw water taken from the North Saskatchewan River (NSR) and Driedmeat Lake (DML). Ozonation dosages were selected relative to NVDOC content, and the effects of pH, alkalinity and ozone dose on DBP production were determined in factorial experiments as described in Section 5.2. Appreciable alkalinity in these samples precluded obtaining data at the lower level used in previous experiments (0 mg/L alkalinity). These effects were compared with those observed for ozonation of isolated fulvic acid fractions (Sections 5.1 and 5.2) to determine if the natural water matrix influenced these effects in ways other than those observed with the various fractions. The influence of non-fulvic-acid precursor material present in the natural water matrix was also considered by comparing DBP yields obtained to those resulting from the ozonation of NOM fractions.

5.3.1 Natural Water Characteristics

Both river and lakewater samples were obtained under winter conditions. These conditions were directly comparable to those in which the fulvic acids were isolated from the North Saskatchewan River. NVDOC concentrations for both sets of samples were

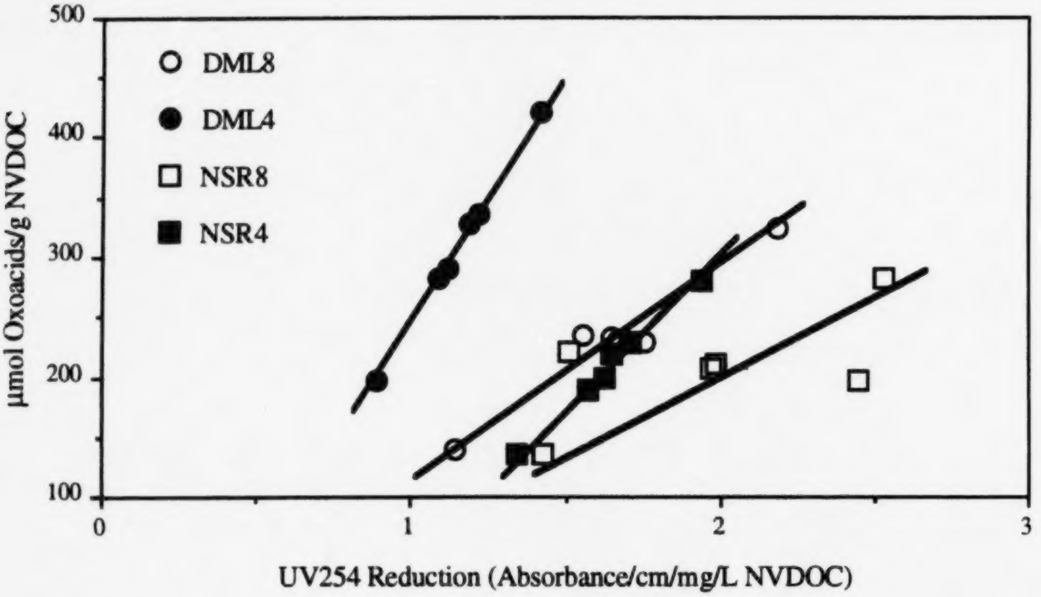


Figure 5.17 Correlations Between UV Reduction and Oxoacids Production on Ozonation of Various Fractions of NOM at 5 mg/L NVDOC (L = lakewater source, R = river water source, 8 = XAD-8, 4 = XAD-4)

similar at 1.34 and 1.67 mg C/L. The lakewater NOM was isolated during the fall and therefore may have differed slightly in character than the raw water obtained in winter. However the lakewater source had a similar NVDOC content to that measured when NOM fractionation was in progress (17.2 *vs* 16.4 mg C/L). Therefore the raw sample and isolated NOM were considered to be comparable in fulvic acid characteristics.

Raw water quality data for both sources are shown in Table 5.2. The most notable difference between the two sources was their organic content. The lakewater contained approximately 10 times the NVDOC when compared with the river water (1.67 *vs* 16.35 mg/L NVDOC).

Both sources contained appreciable amounts of dissolved solids, as measured by conductivity. The lakewater source contained approximately twice the conductivity and alkalinity, and 1.5 times the hardness, when compared with the river water source. The pH of both sources was near neutrality, the lakewater source was more basic at pH 7.93.

5.3.2 Effect of pH, Alkalinity and Ozone Dose on UV Absorbance

In order to test whether the natural water matrix would affect colour reduction by ozone (as measured by UV absorbance), the UV absorbance of the natural source waters was determined both prior to and following ozonation using similar conditions to those outlined for the isolated fulvic acids in previous sections. Samples were buffered to pH 6 or 8, alkalinity was either increased by 200 mg/L as $CaCO_3$ or left at ambient levels and ozone dosages of 1:1 and 3:1 ozone:NVDOC mass ratio were used. Midpoints of these conditions were also employed and were used to determine the significance of the differences in mean effects observed, as described in Chapter 3. UV absorbance was measured at 254 nm.

The effects of pH, alkalinity and ozone dose were similar regardless of the water source or its NVDOC concentration (Figure 5.18). For both the lakewater and river water samples, there was a 20 to 25 % greater reduction in UV absorbance at pH 8 than at pH 6.

Table 5.2 Characteristics of Waters Obtained from the North Saskatchewan River and Driedmeat Lake*

Parameter	N. Sask. River	Driedmeat Lake
Temperature at Time of Collection (°C)	1.0	1.5
pH	6.95	7.93
NVDOC (mg C/L)	1.67	16.4
Total Alkalinity (mg/L as $CaCO_3$)**	144	304
Conductivity (µS)	130	280
Total Hardness (mg/L as $CaCO_3$)	190	228

* North Saskatchewan River was sampled January 15, 1993. Driedmeat Lake was sampled January 27, 1993.

** Primarily bicarbonate alkalinity for both sources.

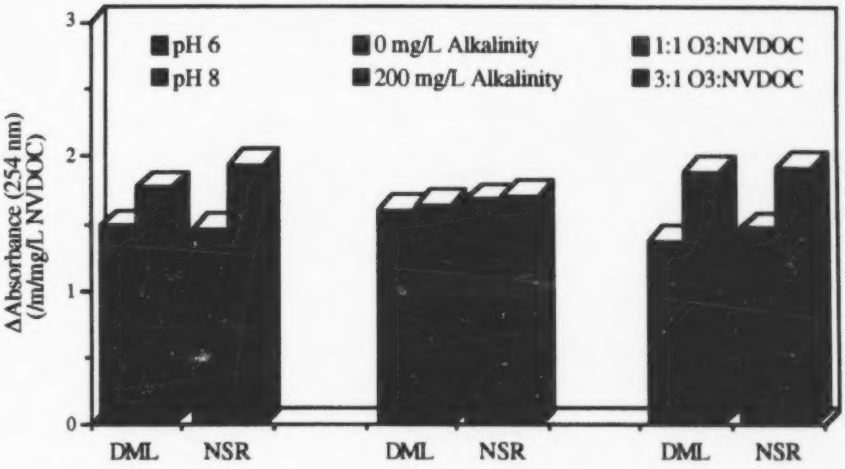


Figure 5.18 Effect of pH, Alkalinity and Ozone Dose on Reduction of UV Absorbance of Natural Source Waters (DML = lakewater source, NSR = river water source; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

A similar reduction was observed when the ozone dose was increased *from 1:1 to 3:1* ozone:NVDOC. Alkalinity effects were negligible for both samples, although it must be remembered that the alkalinity in both of these samples was relatively high prior to commencing the experiment (144 and 304 mg/L as $CaCO_3$).

Results were similar to those observed from the ozonation of corresponding fulvic acid fractions in reagent water (Section 5.2.1). The fulvic acids displayed greater UV reductions at the higher pH and ozone dose, and alkalinity was not considered to be a factor. The magnitudes of the effects, however when comparing natural water matrices to isolates were different. Colour removal for isolated fulvic acids typically increased by in the range of 10 to 60 % when pH was increased from 6 to 8, whereas corresponding colour removal for the ozonated natural waters was in the range of 20 to 25 %. Ozone dose effects were much more marked for the isolated fulvic acids (45 to 100 % reductions) than for the natural waters (20 to 25 %).

The general agreement in the trends of the observed effects during ozonation of natural and synthetic waters implied that sample components which remained unidentified or were not isolated during fulvic acid isolation did not seriously affect the application of the results of the experiments performed with the isolated fulvic acids. Use of fulvic acids isolates in previous experiments thereby were shown to provide an accurate surrogate for the modelling of general colour reduction subsequent to ozonation.

Differing magnitudes in the major effects could be a result of one or more causes. For example, pH-alkalinity interactive effects (Section 5.1.4) might be partially responsible since both waters exhibited high alkalinity. The presence of natural alkalinity could not easily be reduced for the ozonation experiments of natural waters, only increased, therefore an examination of DBP production at low alkalinity was not possible. Other sample matrix effects not tested (organic and inorganic effects, presence of natural phosphates), or the presence of coloured material not represented by the fulvic acids (humic acids, for example) could also cause changes in the magnitudes of the effects observed.

5.3.3 Aldehyde, Oxoacid and Carboxylic Acid Production

The potential for two natural source waters to produce organic DBPs following ozonation was examined using similar conditions as employed for isolated fulvic acids outlined in previous sections. Samples were buffered to pH 6 or 8, alkalinity was either increased by 200 mg/L as $CaCO_3$ or left at ambient, and ozone dosages of 1:1 and 3:1 ozone:NVDOC were applied. Experimental conditions representing midpoints were also employed. Data for aldehydes, oxoacid and carboxylic acid formation were calculated on a molar basis and summed for each class of by-product to determine if class-specific effects were evident.

Aldehydes and carboxylic acids formed the majority of the by-product classes studied relative to the oxoacids (Figures 5.19 to 5.21). This is shown by the large range for yields on the y axis of the aldehyde plot when compared to the others. Similar results were described in Section 5.1.2 for both water sources when using an NVDOC concentration of 20 mg/L. There are at least two possible explanations for these relative abundances. One is that as portions of the fulvic acids are progressively oxidized from aldehydes to carboxylic acids, in the process some become multiply oxidized to oxoaldehydes, oxoacids and others prior to being oxidized further to simple carboxylic acids. In this case, the relative abundances of the different classes may indicate the relative activation energies for formation of oxoacids, aldehydes and carboxylic acids from precursor materials, for example fulvic acids. It is also possible that different types and amounts of precursor materials are available for oxidation, especially for ozonation of natural water.

It is interesting to note that the yields of aldehydes and carboxylic acids, normalized to NVDOC, were different for the two water sources and that the source with the higher organic content appeared to produce lower yield of these DBPs. In experiments with fulvic acids at either high or low NVDOC concentrations, the yields of aldehydes and oxoacids were observed to be independent of the fulvic acid source *i.e.* were similar for both river

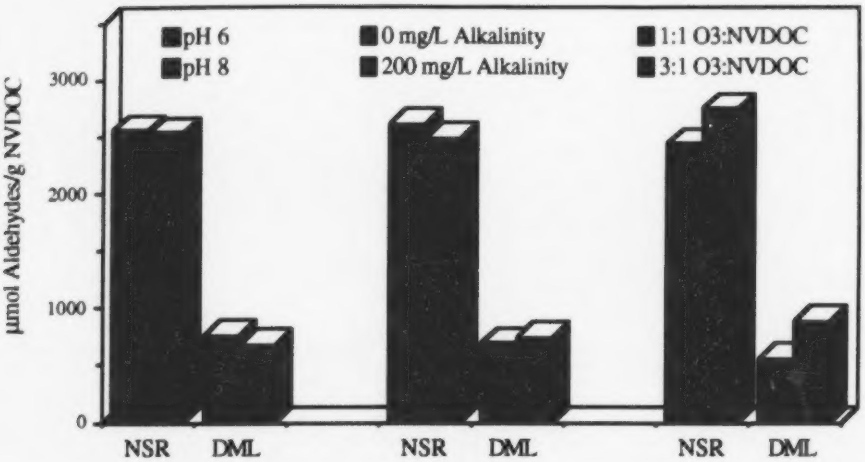


Figure 5.19 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Aldehydes During Ozonation of Natural Waters (NSR = river water source, DML = lakewater source; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose)).

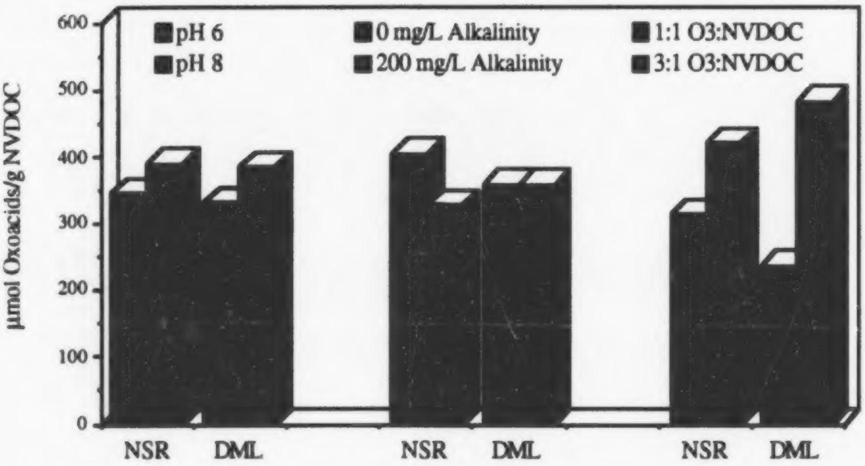


Figure 5.20 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Oxoacids During Ozonation of Natural Waters (NSR = river water source, DML = lakewater source; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose)).

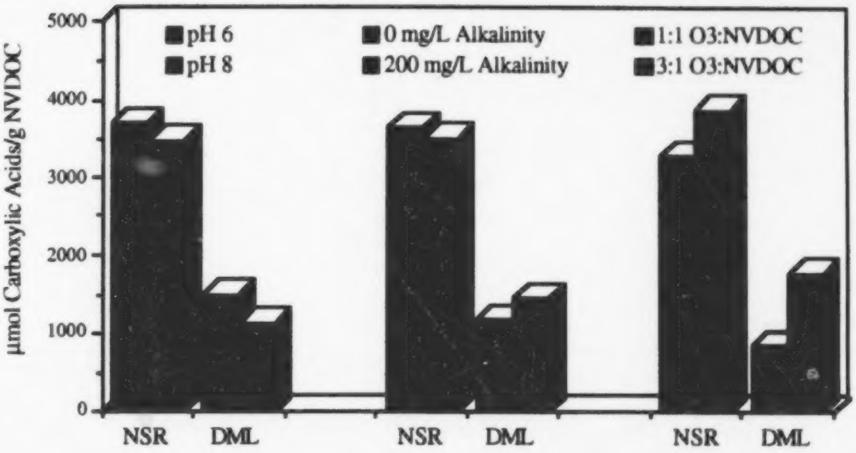


Figure 5.21 Mean Effects of pH, Alkalinity and Ozone Dosage on the Formation of Carboxylic Acids During Ozonation of Natural Waters (NSR = river water source, DML = lakewater Source; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose)).

and lakewater derived fulvic acids. Therefore this result seemed contradictory to those previously obtained. The carboxylic acid yields from the fulvic acids experiments were higher for the lakewater, however. With natural water they were higher for the river water.

When examining the production of aldehydes, results observed with the natural waters may be due in part to the concentration effect to be described in Chapter 6. If one considers that approximately 40 % of the NVDOC is fulvic acid and assumes that the fulvic acids are the major precursors for aldehydes, then the aldehyde yields for the ozonated river and lake waters can be recalculated on a per-gram-as-fulvic-acid basis to be approximately 6000 (river) and 1500 (lakewater) µmol aldehyde/gC as fulvic acid. Yields of aldehyde from fulvic acids at similar NVDOC were approximately 1500 µmol/g NVDOC from lakewater fulvic acid (20 mg C/L NVDOC) and between 4000 and 6000 µmol/g NVDOC for the river water (5 mg C/L NVDOC). These calculations support the theory that the yield differences may be due to concentration effects, and may also indicate that the major precursor materials for aldehydes are the fulvic acid and hydrophilic base fractions of NOM described in Section 5.2.

Similar calculations regarding carboxylic acid yields do not result in the same concentrations, and the yields of carboxylic acids in natural water far exceed those predicted by ozonation of fulvic acid. Concentration effects likely influence the yields, however it is probable that the major carboxylic acid precursors are not fulvic acids but some other chemical species.

The fact that oxoacid yields were similar for the two water sources (normalized to NVDOC) is also interesting and may indicate that these species are intermediates in ozonation reactions. For example, for a two-step reaction involving an intermediate where the first step is rate-limiting and the second step is very fast, the concentration of the intermediate species is often low and nearly constant throughout the reaction period (March, 1968). In kinetic studies of such reactions, this steady state is often assumed for the intermediate to facilitate the determination of the reaction rate constants. Similar yields were also obtained for the ozonation of fulvic acids alone (Sections 5.1 and 5.2) indicating that these species may contribute significantly to oxoacid formation. This also supports the idea that oxoacids may be intermediate species in the ozonation of NOM.

In relation to the other classes of DBPs, oxoacid yields represented 10 to 15 % of those of the other compound classes for the river water and 50 to 75 % for lakewater. Aside from the possible presence of different precursors in the two types of water or a possible as yet unconsidered matrix effect, the difference in yields of oxoacid from the two sources relative to those obtained from fulvic acid ozonation may be a result of alkalinity effects. The alkalinity of the lakewater was much higher than that of the river water (304 *vs* 144 mg/L as $CaCO_3$, respectively), and alkalinity promotes formation of oxoacids from fulvic acids at high pH and ozone dose (Figure 5.9).

When considering the influence of the various ozonation parameters which were examined, pH effects were generally much less pronounced for the ozonation of natural waters than were observed for the ozonation of fulvic acids, however the trends were similar. The effect of pH on aldehyde and carboxylic acid formation (Figures 5.19 and 5.21) was different from that on oxoacid formation (Figure 5.20). Formation of aldehydes and carboxylic acids was favoured at low pH while that of oxoacids proceeded with greater yield at pH 8. This effect can be explained by making reference to the mechanisms of molecular ozone reaction as discussed in Section 5.1.2.

Alkalinity exerted a much smaller effect on DBP production than did pH. In general at a higher alkalinity decreased DBP formation as observed for all three classes of by-products. A few instances of increased production at higher alkalinity were noted, but the magnitudes of all alkalinity effects were such that they were usually within experimental error. The variability in alkalinity effects may be attributable to the experimental conditions which represented intermediate conditions between causing aquatic NOM to be scavengers or promoters of radical reactions. Therefore, in some instances the alkalinity suppressed radical formation and in others the promoting aspect of the aquatic NOM was enough to overcome the inhibitory effects of the alkalinity with regard to DBP production.

The parameter influencing by-product formation to the greatest extent was ozone dosage. Increasing the applied ozone dosage from 1:1 to 3:1 mg ozone:mg NVDOC resulted in higher yields of all by-products. The effect was less pronounced for the formation of aldehydes and carboxylic acids (Figures 5.19 and 5.21) than for oxoacids (Figure 5.20) and was, in general, smaller for river water NOM than for lakewater NOM. It may be that because of the specificity of the molecular reaction, sites of unsaturation react quickly with molecular ozone to form aldehydes and carboxylic acids even at lower ozone doses. As has been stated, these sites react preferentially with molecular ozone. The greater ozone dosage effects observed for oxoacids formation may be due to a possible radical promoting ability of this class of compounds. This may also be related to the large dose effects observed for UV absorbance reduction on ozonation of fulvic acids.

5.4 Summary

At 20 mg/L NVDOC and for the ozonation parameter values studied, it was apparent that the fulvic acids may have reacted both as radical scavengers and promoters, and that the transition between the two states might lie between ozone:NVDOC dosage ratios of 1:1 and 3:1 ozone:NVDOC. pH was shown to be the parameter having the greatest influence on ozonation DBP yields, with greater yields of aldehydes and carboxylic acids being obtained at pH 6 than at pH 8. The influence of pH on the formation of oxoacids and UV absorbance reduction was different than for aldehydes and carboxylic acids, possibly because of this participation in different reaction mechanisms (molecular *vs* radical). UV reduction did not correlate well with oxoacid production at the higher NVDOC concentration, but correlated well at the lower NVDOC concentration. Also, DBP formation characteristics were somewhat site specific in that lakewater ozonation produced higher levels of carboxylic acids whereas IHSS river water NOM ozonation produced greater quantities of aldehydes.

The interactive effects between the ozonation variables pH and alkalinity were studied at the higher NVDOC concentration (20 mg/L). Maximum aldehyde formation was observed at minimum pH and maximum alkalinity, whereas oxoacids were formed in greater quantities at high pH and alkalinity. At the lower ozone dose (1:1 ozone:NVDOC mass ratio), there was an apparent minimum aldehyde formation, and pH-alkalinity interactions were almost a non-effect. The interaction and synergistic effects of pH and alkalinity were most pronounced at the higher ozone dosage examined (3:1 ozone:NVDOC mass ratio).

The effects of the ozonation parameters determined at 5 mg/L NVDOC were similar to those observed at 20 mg/L NVDOC. Therefore, similar reaction mechanisms should apply. The parameter that was observed to affect NOM ozonation by-product formation to the greatest extent was pH. As at 20 mg/L NVDOC, the effect of pH on aldehyde and carboxylic acid formation was different from that observed for oxoacid formation in that formation of aldehydes and carboxylic acids were favoured at low pH whereas formation of oxoacids proceeded with greater yield at pH 8 (for all but one fraction). Alkalinity had a much smaller effect than did pH, however higher alkalinity resulted in a decrease in by-product formation for all three classes of by-products. A few instances of increased production on increased alkalinity were noted, but the magnitudes of all alkalinity effects were such that they were usually within the experimental error associated with non-effects. Increasing the ozone dosage applied to the lakewater fulvic acids resulted in higher yields of aldehydes, and much higher yields of oxoacids. Slight decreases were noted for carboxylic acids. In contrast, for the river water fulvic acids, changes in ozone dosage at the levels evaluated had little effect on DBP yields except for the oxoacids which approximately doubled on increasing the ozone dose regardless of the water source or NOM fraction.

Similar qualitative results were observed for the ozonation of natural waters. However, the relative yields of some DBPs differed from those obtained in fulvic acid experiments, particularly the carboxylic acids and aldehydes, indicating that there were likely precursors in the natural water for these compounds in addition to the fulvic acids. The yields of oxoacids were similar in both simulated and natural waters, indicating that the fulvic acids may be their major precursor materials.

CHAPTER 6

EFFECT OF NOM CONCENTRATION ON ORGANIC OZONATION BY-PRODUCT FORMATION AND UV ABSORBANCE REDUCTION

Many researchers perform their experiments using reactant concentrations which are as much as several orders of magnitude higher than those encountered naturally in the systems under study in order to facilitate quantitation of products. This approach was also initially employed in the present research, where reactants (fractionated natural organic matter (NOM) and ozone) were employed at concentrations which represented approximately 5 and 10 times those encountered in typical drinking water treatment practice. However, due to various competing reactions, those being studied may occur differently in concentrated and dilute systems, making extrapolation of results obtained at high concentration to ambient concentrations difficult. Therefore, in order to facilitate interpretation of comparison data obtained at different solute concentrations (Chapter 5) and perhaps allow inferences for even lower organics concentrations to be made, is was considered important to investigate the effect of NOM concentration on DBP formation. The data reported herein were considered significant enough to warrant including them as a separate chapter, rather than incorporating them into Chapter 5.

The effect of reactant (NOM, ozone) concentration on DBP formation was evaluated at pH 6 and 8, and at a constant ratio of applied ozone to non-volatile dissolved organic carbon (NVDOC) concentration using lakewater fulvic acids isolated on XAD-8 resin. NOM fractions at NVDOC concentrations of 2.5, 5, 10 and 20 mgC/L were ozonated at a mass ratio of 3:1 ozone to NVDOC and without additional alkalinity. Reduction in UV absorbance was measured, in addition to the production of the ozonation DBPs (aldehydes, oxoacids and carboxylic acids) listed in Table 5.1 of Chapter 5.

6.1 NOM Concentration and UV Absorbance Reduction

The effects of varying NVDOC concentrations on UV absorbance resulting from ozonation in the absence of bicarbonate at a constant ozone:NVDOC ratio of 3:1 are illustrated in Figure 6.1 for ozonation of lakewater fulvic acids. For the NVDOC concentrations examined, greater changes in UV absorbance were observed at pH 8 than at pH 6, which was consistent with results presented in Chapter 5. However the magnitudes of the differences between the UV absorbance reductions at pH 6 and 8 were not constant throughout the NVDOC concentration range (the UV absorbance reduction curves were not parallel). It is evident from these data that colour reduction, measured by change in UV absorbance at 254 nm, was not a linear function of NVDOC concentration, especially at concentrations less than 10 mgC/L. However, the removal efficiency appeared to plateau with increasing NVDOC concentration at between 70 and 80 %, depending on the pH employed. Part of the reason that higher reductions were not achieved may have been because many chemical species absorb UV radiation at or near 254 nm, including some which are by-products of ozonation. Therefore, the UV absorbing species are being created during ozonation, limiting the extent of UV reduction possible.

These observations were consistent with those described by Staehelin and Hoigné, (1985) for the effects of humic acids and other solutes on ozone consumption. They state that humic acids may be responsible for some of the initial "spontaneous ozone consumption" observed in water treatment plants, and that interactions of various solutes with free radicals in solution will result in non-additive effects of various types of ozone reactions occurring. The observations made in the present research indicate that the reaction of ozone at UV absorbing sites of the fulvic acids molecules becomes less prevalent at lower NVDOC concentrations.

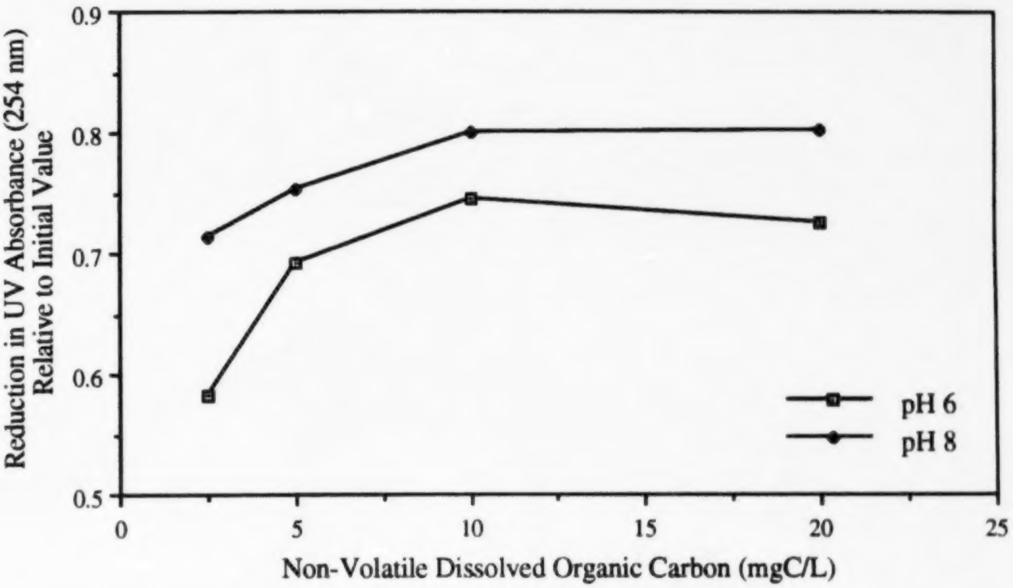


Figure 6.1 Reduction in Lakewater Fulvic Acid UV Absorbance as a Function of NVDOC Concentration and pH (3:1 applied ozone:NVDOC ratio, no added alkalinity, 254 nm)

6.2 Organic By-Product Results

Varying concentrations of lakewater fulvic acid were ozonated at a constant applied ozone:NVDOC mass ratio of 3:1, and the production of aldehydes, oxoacids and carboxylic acids were measured. The tests were performed in the absence of added alkalinity, permitting both radical and molecular reactions to occur, and employed 0.05 M phosphate buffering to pH 6 or 8.

6.2.1 Results of All Classes of DBPs

As was reported for the factorial experiments described in Chapter 5, yields of aldehydes and carboxylic acids were greater at pH 6 than 8, whereas yields of oxoacids were greater at pH 8. Additionally, the greatest concentration effects were observed for aldehyde formation in that the range of concentrations of aldehydes produced was greatest over the range of NVDOC concentrations studied. At low NVDOC concentrations, aldehyde production dominated all other measured DBPs while at higher NVDOC, aldehyde and carboxylic acid concentrations were similar. Except for the relative yields of aldehydes, oxoacids and carboxylic acids, the results obtained at pH 8 were qualitatively similar to those at pH 6. Since the results at the two pH setpoints were similar, only those obtained at pH 6 are discussed in this chapter. The data obtained at pH 8 are shown in Appendix V.

DBP production was not a linear function of NVDOC concentration. Figures 6.2 to 6.5. show the data normalized to their corresponding NVDOC concentrations. While absolute DBP yields (μg/L, μM) increased with increasing substrate concentration (not shown), the increases were not directly proportional to the increases in fulvic acid concentration. If the absolute yields had been directly proportional to NVDOC concentration, then the curves shown in Figures 6.2 to 6.5 would appear as horizontal lines. However, data presented in the figures indicate that higher NVDOC concentrations produced lower DBP yields per gram NVDOC, except for ketomalonic acid (Figure 6.4).

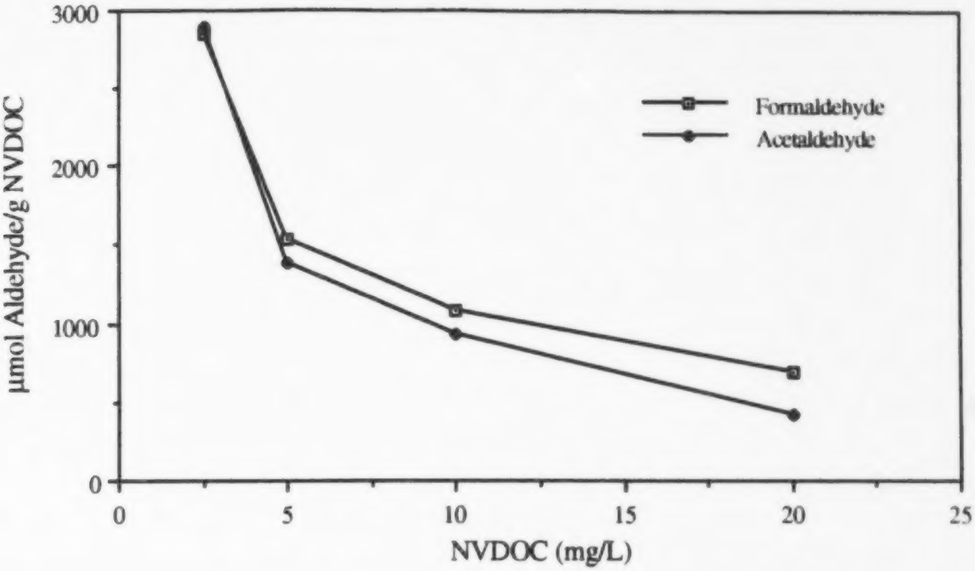


Figure 6.2 Effect of NVDOC Concentration on Formaldehyde and Acetaldehyde Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 6, No Added Alkalinity

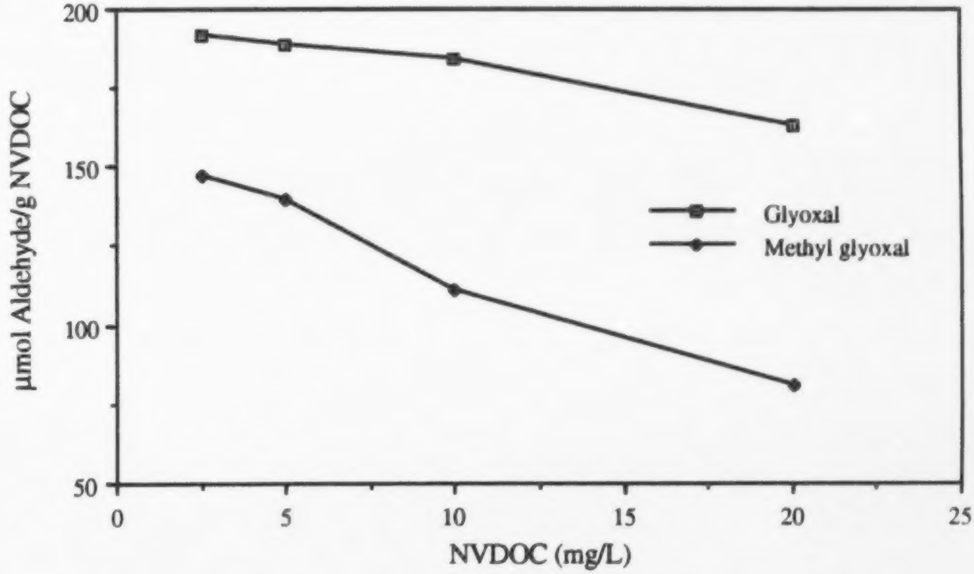


Figure 6.3 Effect of NVDOC Concentration on Glyoxal and Methyl Glyoxal Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 6, No Added Alkalinity

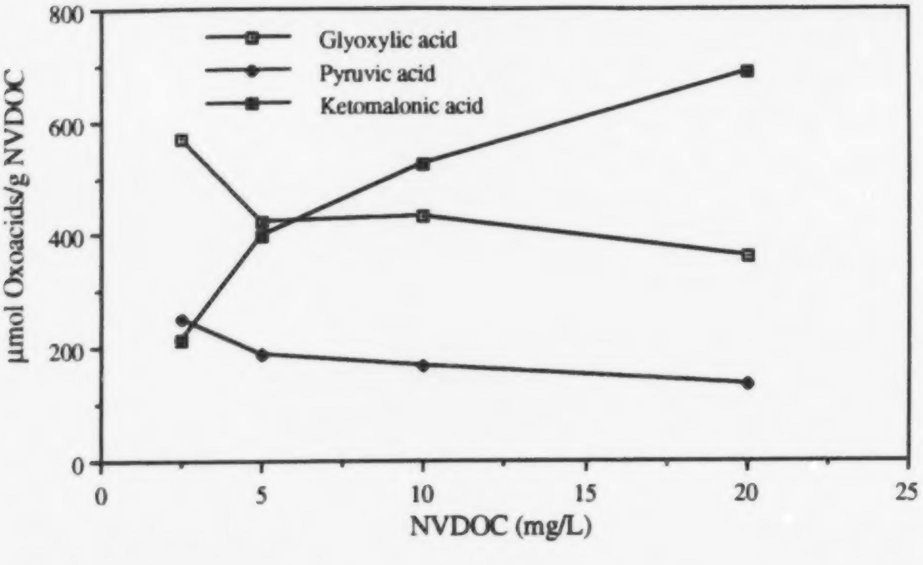


Figure 6.4 Effect of NVDOC Concentration on Oxoacid Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 6, No Added Alkalinity

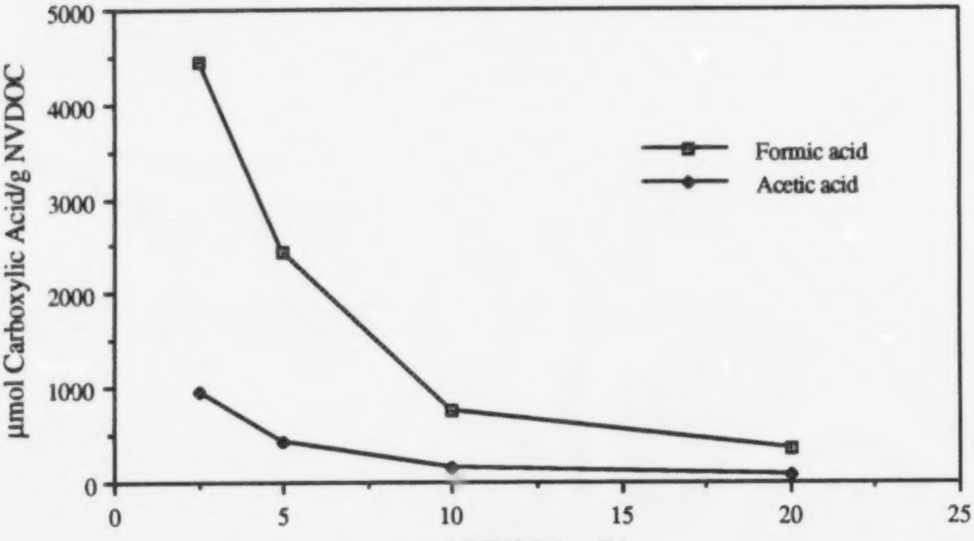


Figure 6.5 Effect of NVDOC Concentration on Carboxylic Acid Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 6, No Added Alkalinity

The reduced concentration effects observed at higher NVDOC concentrations may also be the result of the ozone-quenching ability of the fulvic acids described by Staehelin and Hoigné (1985), as was discussed in relation to UV absorbance reductions described in the previous Section. Various interactions between ozone and solutes or other radicals in solution may have prevented the ozone from reacting with the fulvic acids at the same reactive sites as it did at low NVDOC, and preventing DBP production.

Absolute yields increased for all DBPs with an increase in initial NVDOC concentration and ozone dose at either pH. This result was also observed by Xiong *et al.* (1992) for the formation of glyoxylic acid from the ozonation of a similar fulvic acid at pH 3.4 and a 1:1 mass ratio of ozone:NVDOC, although it is not clear if the concentrations are expressed per mass of fulvic acid or are absolute values. While the present research and that of Xiong *et al.* (1992) cannot be directly compared due to pH and ozone dose differences, the DBP yields appear to be similar to those for both NVDOC concentrations reported, indicating that the results reported by Xiong *et al.* (1992) are probably absolute yields. In their research, they identified glyoxylic acid as a precursor for radical reactions on the basis of the concentration effects noted (higher yield at higher NVDOC, constant 1:1 ozone:NVDOC mass ratio, pH 3.4). Since the same effect was observed for each of the ozonation DBPs studied in the present research, then according to the above rationale all of these DBPs could be precursors for radical reactions. Certainly, each of these species possesses active hydrogens which could participate in free radical reactions. The oxoacids and carboxylic acids in their ionized forms would also react with ozone to promote free radical reactions as described by Hoigné and Bader (1983b) and Staehelin and Hoigné (1985) for formic acid, who also report glyoxylic acid as being an initiator and promoter of free radical reactions. They reported that the rate constant for ozone depletion in the presence of formic acid increased more than linearly with the concentration of formic acid, indicating that ozone reacts with formic acid to produce free radicals. Similar results were observed for the reaction of ozone and glyoxylic acid. Therefore, when ozone reacts with fulvic acids to form species like formate and glyoxylic acid, further ozonation results in the reaction of ozone and these species to form free radical species which react with ozone or with other species present to result in reaction termination.

6.2.2 Ketomalonic Acid Formation

Another interesting result of the present experiments was that observed for the production of ketomalonic acid from the ozonation of lakewater fulvic acids. The toxicology of ketomalonic acid is as yet unknown, but it has been suggested to be a possible surrogate compound for that part of the biodegradable organic material known as assimilable organic carbon, or AOC (Xie and Reckhow, 1992) and therefore is of interest from a distribution system biological stability point of view.

The production of this oxoacid, normalized to NVDOC concentration, increased more than linearly with increasing NVDOC, as is shown in Figure 6.4. This appears to be more indicative of free radical-promoting capability than a simple increase in absolute yield, as was observed for the other DBPs. Alternatively, this could also indicate that ketomalonic acid is a product of the free radical reactions which were increased at higher NVDOC concentrations as predicted by Staehelin and Hoigné (1985) and Xiong *et al.* (1992).

This effect may actually be a result of the mechanism by which ketomalonic acid is formed, and suggests a possible precursor material for it, namely a semiquinone-type moiety known to be present within the fulvic acid microstructure. Senesi *et al.* (1977) demonstrated that redox reactions of aqueous fulvic acids are reversible and proceed *via* semiquinone intermediates as shown in Figure 6.6. Wilson and Weber (1977) studied the equilibria of semiquinones and their protonated forms by electron spin resonance (ESR) and found an exponential relationship between pH and spin content (roughly correlated with free radical content). The free radical contents of fulvic acids have often been ascribed to quinone, semiquinone and hydroquinone moieties, which would make them ideal targets

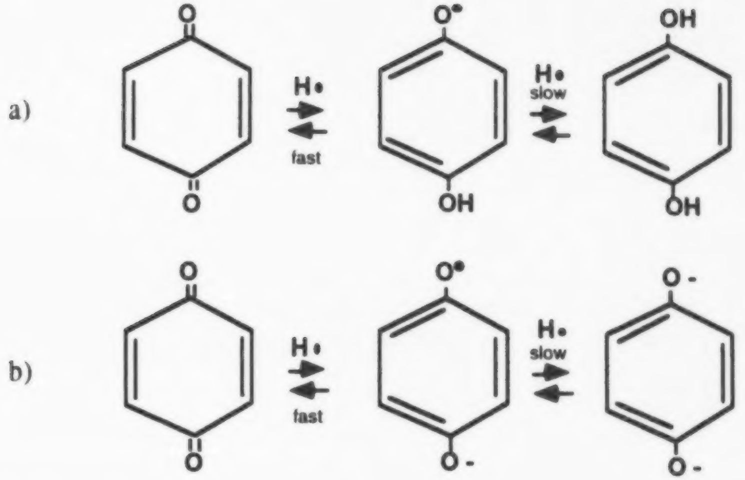


Figure 6.6 Aqueous Redox of Quinone-Type Moieties of Fulvic Acids Showing Semiquinone Intermediates. a) Acidic or Neutral pH; b) Basic pH (Adapted from Senesi *et al.*, 1977 in Hayes *et al.*, 1989a, pp. 396)

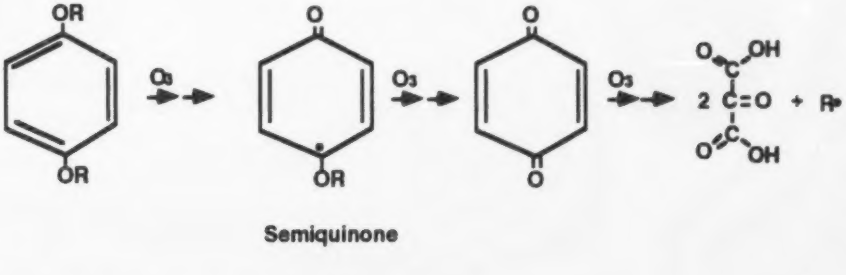


Figure 6.7 Proposed Reaction Scheme for the Formation of Ketomalonic Acid from Fulvic Acid

for attack during ozonation, especially under conditions favouring free radical processes.

It is hypothesized that ketomalonic acid may be formed from the reaction of ozone and semiquinones in fulvic acid, and that the stoichiometry favours the production of two oxoacids per semiquinone. This hypothesized reaction is illustrated as shown in Figure 6.7 and may explain the observed concentration effects. Pre-oxidation of phenoxy groups to their semiquinones is also included in the reaction scheme. Although it was not possible during the present research, experiments with model compounds could be used to determine the products formed and the stoichiometry of the reaction. Consultation of the literature with regard to the viability of this reaction was inconclusive.

6.3 Summary

The foregoing emphasizes one of the problems involved in extrapolating bench scale data, often obtained at higher than ambient reactant concentrations, to real situations. It has long been recognized that DBP formation cannot be predicted globally, *i.e.* for several source water types, from data not obtained at those sites due to differences in source water characteristics. The data presented herein, generated in the absence of added bicarbonate, show that even if such data are available for a given site, it may be difficult to predict DBP formation for that site under varying NVDOC concentrations. In particular, if such data are extrapolated to NVDOC concentrations lower than those on which the database was formed, both the extent of colour reduction (as measured by UV absorbance) and DBP formation can be seriously underestimated.

If these results are interpreted according to the reports of other researchers, then all of the DBPs studied could be considered precursors of free radical reactions. This may be especially true for one oxoacid, ketomalonic acid, which was different from the other DBPs in that its production increased much more dramatically with increasing NVDOC concentration. The observations regarding this oxoacid also lend support to a hypothesized reaction scheme for the formation of ketomalonic acid from quinone-type precursors in the fulvic acid complex. Should it prove to be correct, knowledge of its precursor would be useful for controlling the production of this DBP by providing clues to finding methods which might be successful for reducing their concentration. This would be important whether or not ketomalonic acid is found to contribute significantly to AOC, and may also be prudent if toxicological studies indicate it to be harmful.

CHAPTER 7

EFFECTS OF OZONATION ON THE FORMATION OF HALOGENATED DBPS FROM CHLORINATION OR CHLORAMINATION

The half life of ozone is very short, of the order of minutes under typical drinking water treatment conditions (as little as 7 minutes; Gilbert *et al.*, 1990), and as such utilities employing ozone for disinfection will be required to use an additional disinfectant for maintenance of a residual in the distribution system. This will typically be accomplished by addition of either chlorine or chloramines. The chlorination and, to a lesser extent, chloramination of humic materials has been studied in considerable detail by others (Jolley *et al.*, 1978-1990; AWWA Reports; Reckhow and Singer, 1990), and recently the effects of ozonation prior to chlorination have also been investigated (Reckhow and Singer, 1986, 1990; Coleman *et al.*, 1992). The purpose of this part of the present research was not to repeat those experiments, but to determine the differences in DBP production resulting from ozonation of the different NOM fractions and to compare the results with those from the ozonation and chlorination or chloramination of the respective natural waters.

In this set of experiments, chlorine or chloramine was added to ozonated and non-ozonated fulvic acid solutions to measure the impact of ozonation conditions on subsequent oxidant demand and halogenated disinfection by-product (XDBP) formation. The pH and alkalinity of the test solutions were not altered from their values in the ozonation experiments, representing the simplest possible treatment scenario which may be encountered in combined disinfectant strategies.The experimental protocol following ozonation also could yield the greatest concentrations of XDBPs since biological or physical (adsorption) treatment was not included. Thus the effects of pH and alkalinity discussed herein refer to the combined effects observed during ozonation and subsequent chlorination or chloramination. Natural source waters and solutions of fractionated NOM were employed to allow comparisons of the relative importance of the various ozonation parameters on individual precursor materials to be made as well as to attempt to evaluate effects of the natural water matrices. Halogenated DBPs which were routinely measured included trihalomethanes (THMs), haloacetic acids (HAAs), chloral hydrate and cyanogen chloride as shown in Table 7.1. However, due to analytical equipment availability constraints, only selected NOM fractions could be investigated for XDBP formation characteristics. Chlorine/chloramine demand was measured on a number of fractions.

For the following discussion, the variance of the replicated midpoints in each experiment was calculated and used to aid in the identification of significant parameter effects as described in Chapter 3. The resulting confidence intervals are tabulated in Appendices VI and VII, rather than complicating the text by including this statistical data in the discussion of each comparison. In general, parameter effect differences of more than approximately 10 % were statistically significant at the 90 % or 95 % confidence level. Therefore, a 10 % difference criterion may be used by the reader as a guide in identifying significant effects.

7.1 Post-Ozone Chlorination

Chlorine has historically been the distribution system disinfectant of choice in North America, and therefore its reaction with previously ozonated natural organic matter (NOM) was an important consideration in this research. Selected samples of ozonated NOM, as generated in experiments described in Chapter 5, were chlorinated with reagent grade sodium hypochlorite at a 3:1 molar ratio of Cl_2:organic carbon (as NVDOC) to determine the effects of ozonation parameters on formation potentials for some common XDBPs. The pH and alkalinity of the test solutions were not altered from their values in the ozonation experiments, and following chlorination, the samples were incubated at room temperature (nominally 20 °C) in the dark for 7 days. Halogenated by-products examined in this part of the investigation are listed in Table 7.1.

Table 7.1. Halogenated Disinfection By-Products

Class	Compound
Trihalomethanes	Chloroform
	Dichlorobromomethane
	Dibromochloromethane
	Bromoform
Haloacetic Acids	Dichloroacetic acid
	Trichloroacetic acid
Miscellaneous	Chloral hydrate
	Cyanogen chloride

7.1.1 Effects of Ozonation Parameters on Oxidant Demand

The effects of pH on the subsequent chlorine demand of five NOM fractions are illustrated in Figure 7.1. The effects of alkalinity and ozone dosage were within experimental error of being non-effects and therefore are not shown.

The greatest pH effect was noted for the hydrophilic bases fraction isolated on AG MP-50 ion exchange resin. The demand at pH 6 was approximately 3 times that observed at pH 8, possibly due to the reaction of hypochlorous acid with amino groups to form organochloramines. For example, N-chlorination has long been known or suspected to be the initial step in the formation of formaldehyde from glycine and chlorine (Dakin, 1916).

The effects of pH on chlorine demand with AG MP-50 fractions were unique in that slightly greater demands were observed at pH 8 for many of the other fractions. The greater extent of reaction at pH 8 as compared to pH 6 may be related to the nature of reactions known to occur with fulvic materials. For example, reactions in which hypochlorite reacts at carbons *alpha* to carbonyl groups in the molecules (part of the mechanism of the haloform reaction, discussed in the next Section) are known to occur at higher pH values.

The general absence of alkalinity effects in chlorination reactions was expected and is not shown. However, given that XDBP formation following ozonation and chlorination can proceed by the pathway described above and that ozonation increases the carbonyl content of NOM, the lack of ozone dosage effects might indicate that a plateau for carbonyl formation was reached at some ozone dosage at or less than 1:1 ozone:NVDOC.

The XAD-4 and hydrophilic base fractions, which have not yet been extensively tested by others may contribute significantly to the chlorine demand of natural waters. The chlorine demands associated with the XAD-4 isolated fractions were 75 to 100 % greater than those observed for the XAD-8 isolated NOM, and that of the hydrophilic base fraction was as much as 4 times as great (Figure 7.1). Inclusion of these fractions could contribute

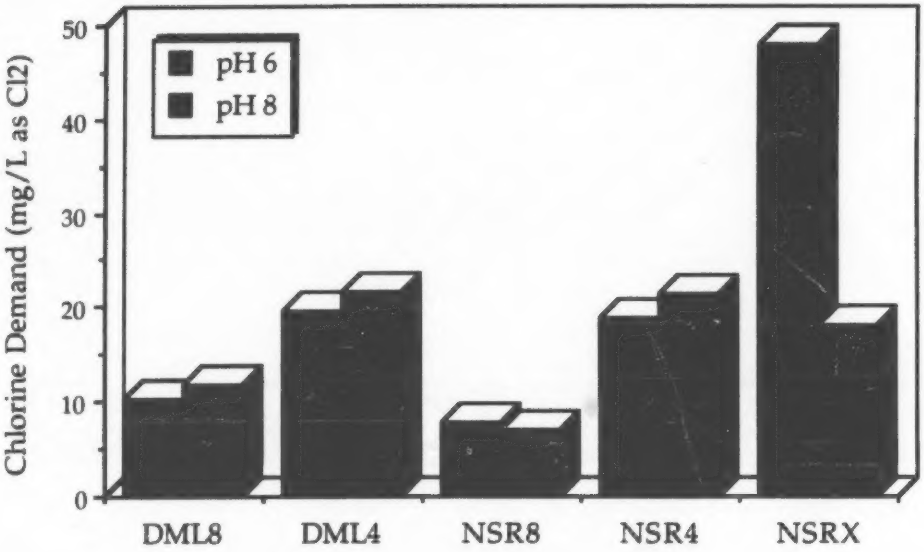


Figure 7.1 Effect of pH on the Chlorine Demand of Ozonated NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

significantly to any of the previously reported models involving humics chlorination and possibly to the study of XDBP formation.

As was discussed for the formation of aldehydes in Chapter 5, some consideration should be given to the differences in the mean molecular weights of the two types of NOM fractions when rationalizing the greater quantities of XDBPs which were produced from the XAD-4 fractions than the XAD-8 fractions. Equal mass concentrations of the two types of NOM might be expected to result in higher molar concentrations of precursor material for the lower molecular weight fraction.

Overall effects of ozonation on chlorine demand are illustrated in Figure 7.2. These data represent the average of results obtained at 1:1 and 3:1 ozone:NVDOC mass ratios subtracted from values obtained for NOM not undergoing ozonation. Relative to non-ozonated material, ozonated fractions generally displayed decreased chlorine demand. The greatest reductions were for the fractions isolated on XAD-8 (more aromatic, higher molecular weight). These large reductions may be explained by recognizing that ozone reacts at sites of unsaturation to deactivate them from subsequent reaction with chlorine. The moderate reduction exhibited by the AG MP-50 fraction may be a result of oxidation of amino groups to organic nitro-compounds or to nitrate, removing amino groups which might react with chlorine to form chloramines.

7.1.2 Effects of Ozonation Parameters on XDBP Formation Potential

Halogenated disinfection by-products (XDBPs) which were measured for this part of the study are listed in Table 7.1. Of all possible trihalomethane species, only chloroform and dichlorobromomethane were detected (in cases where dichlorobromomethane was detected, it was typically at a concentration less than 3 % of that of chloroform). Of all potential haloacetic acid isomers, only di- and trichloroacetic acid were measured. These are the HAAs of greatest recent health concern and were those comprising greater than 90 % of the total HAAs detected (as estimated from gas chromatographic peak areas). Some

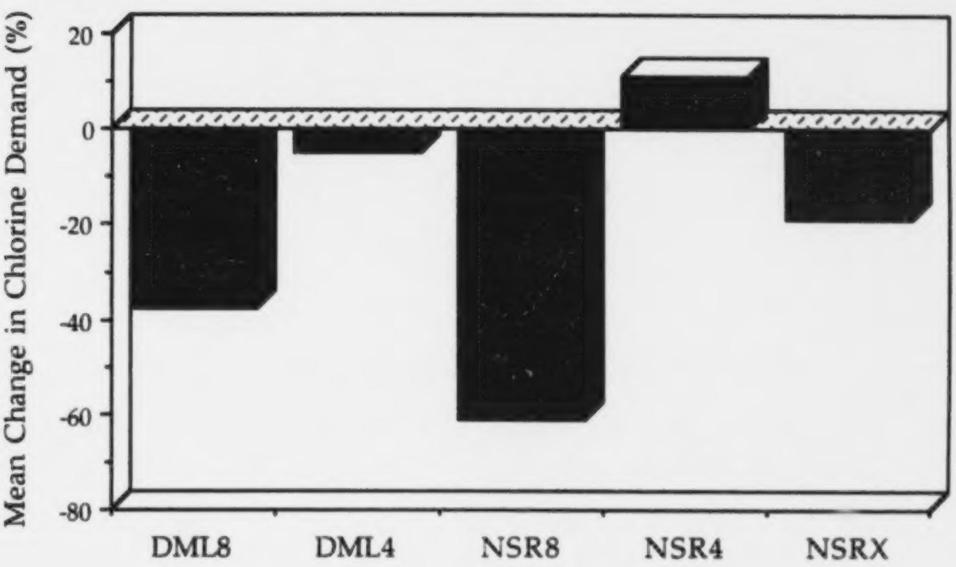
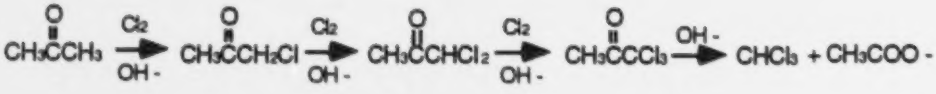


Figure 7.2 Changes in Chlorine Demand on Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4, X = AG MP-50)

brominated XDBP analogues are also of health concern, but it was not within the scope of this research to include them. Due to analytical equipment availability constraints, only selected NOM fractions could be investigated for XDBP formation characteristics. Details are reported in the relevant sections as necessary.

Trihalomethanes are among the most widely studied XDBPs, and an investigation of the present type would be incomplete without some reference to them. The effects of pH, alkalinity and ozone dosage on total trihalomethane formation potential (THMFP) for lakewater NOM isolated on XAD-8 and XAD-4 resin are illustrated in Figures 7.3 to 7.5.

The greatest effects on THMFP were observed for changes in pH, regardless of whether or not ozone was applied (Figure 7.3). The greatest pH effect was observed for ozonated and subsequently chlorinated samples for which THMFP at pH 8 was approximately twice that at pH 6. Even at the lower THMFP levels encountered when chloramines were employed (Section 7.2.2), THMFPs determined at pH 8 were greater than those obtained at pH 6. This observation is in agreement with the literature. For example, Boyce and Hornig (1983) show that base catalyzed chlorination (electrophilic substitution) and subsequent hydrolysis of model compounds to form trihalomethanes can proceed in some instances similarly to the haloform reaction (shown below).



$$CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[OH^-]{Cl_2} CH_3\overset{O}{\overset{\|}{C}}CH_2Cl \xrightarrow[OH^-]{Cl_2} CH_3\overset{O}{\overset{\|}{C}}CHCl_2 \xrightarrow[OH^-]{Cl_2} CH_3\overset{O}{\overset{\|}{C}}CCl_3 \xrightarrow{OH^-} CHCl_3 + CH_3COO^-$$

One might expect that ozonation could increase the amount of THM precursor by oxygenating portions of fulvic acid to similar structures.

However there are known THM precursors which react with chlorine at neutral pH, employing electrophilic substitution mechanisms involving HOCl which are faster than those involving OCl^-. 3,5-dihydroxybenzoic acid is one such precursor, and similar structures are known to be present in fulvic acids. This compound reacts quantitatively

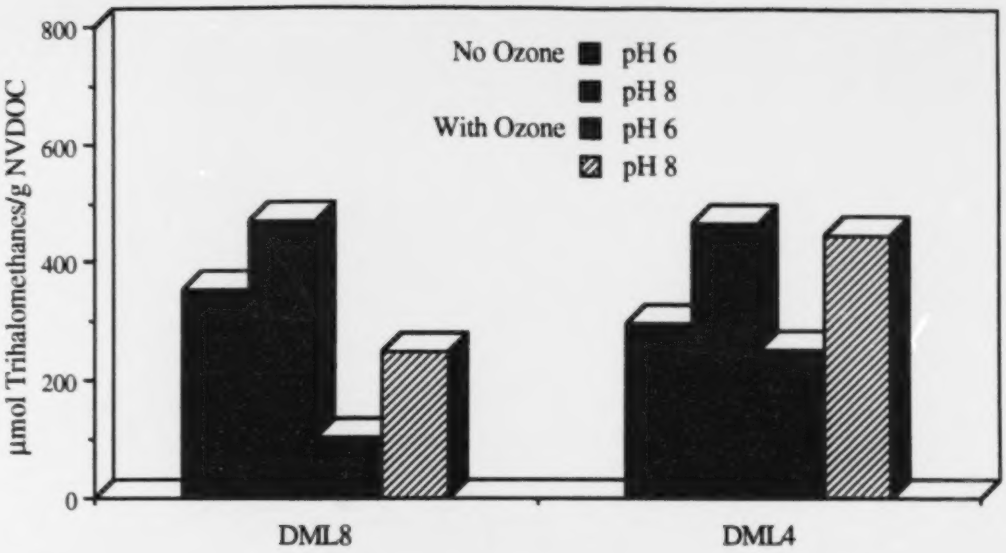


Figure 7.3 Effect of pH on the Formation of Trihalomethanes from the Ozonation of NOM Fractions (2:1 O_3:NVDOC; DML = Driedmeat Lake, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

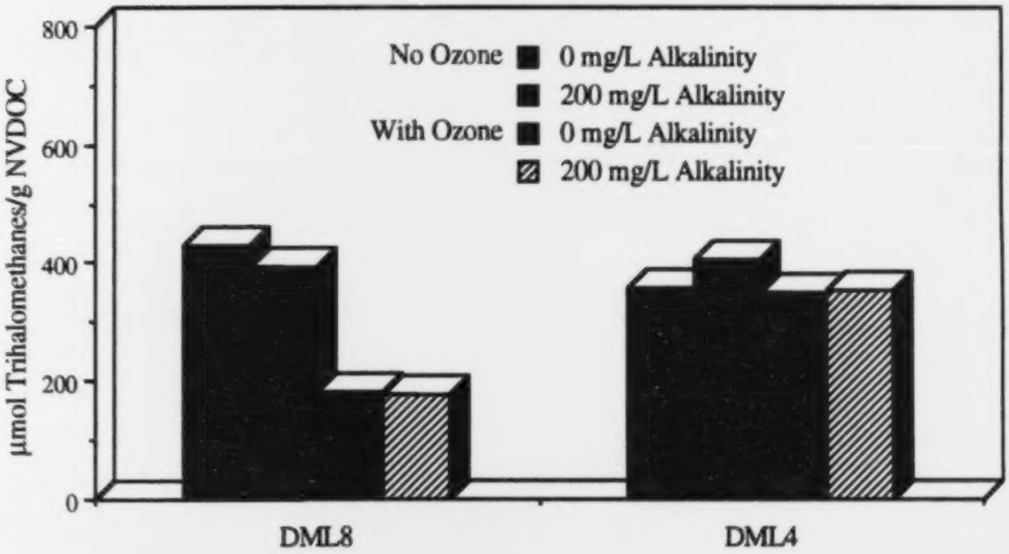


Figure 7.4 Effect of Alkalinity on the Formation of Trihalomethanes from the Ozonation of NOM Fractions (2:1 O_3:NVDOC; DML = Driedmeat Lake, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and dose))

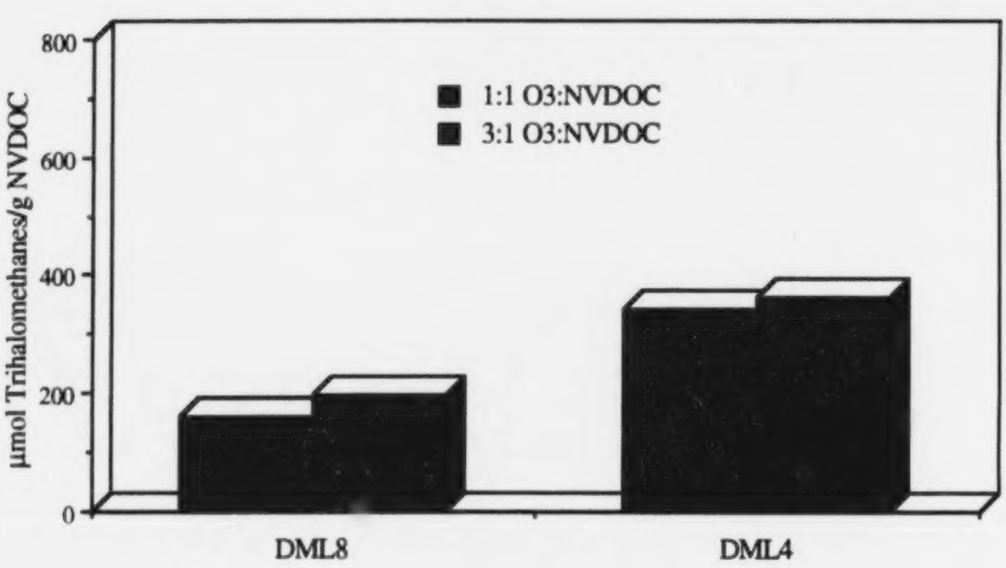


Figure 7.5 Effect of Applied Ozone Dose on the Formation of Trihalomethanes from the Ozonation of NOM Fractions (DML=Driedmeat Lake, 8=XAD-8, 4=XAD-4; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

with chlorine at pH 7 to produce chloroform, and is used as a quality control measure in the THMFP test described in Standard Methods (Method 5710 B, APHA-AWWA-WEF, 1992). Resorcinol (3,5-dihydroxybenzene) also reacts with chlorine at pH 6 to produce chloroform in good yield (Boyce and Hornig, 1983) however yields at pH 8 are higher. These types of compounds would be expected to react with ozone, altering them from future participation in THM formation thereby resulting in reduced THMs on ozonation. This could explain why some researchers, for example Boyce and Hornig (1983), Bedessem *et al.* (1990) and Coleman *et al.* (1992), each found instances where opposite pH effects were observed.

Alkalinity did not significantly affect THMFP results, except for some NOM samples which were chlorinated in the absence of pre-ozonation. In these cases, higher alkalinity reduced THMFP, but typically by less than 10 percent.

Similar pH and alkalinity effects were observed for both derived NOM fractions (XAD-8, XAD-4) and natural waters (Appendix VI). As well, similar THM yields were obtained for both fractions prior to ozonation. Following ozonation, however, THM yields from the XAD-8 fraction were approximately 50 % less than for the corresponding non-ozonated fulvic acid or for the XAD-4 fraction. These results can be explained by the relative aromatic and carboxyl contents of the two materials. The XAD-8 material contained higher aromatic content, and some aromatic moieties have been shown to be THM precursors as discussed above. Ozone reacted with these to reduce the THMFP. The XAD-4 fulvic acids are more aliphatic in nature. The THM precursors removed from the XAD-8 NOM are not present in as great a quantity in the XAD-4 NOM.

The optimum ozone dosage for THM precursor reduction appears to be at less than a 1:1 applied ozone:NVDOC ratio, at least for lakewater NOM isolated on XAD-8 resin. The XAD-4 fraction showed no reduction in THMFP on ozonation (Figures 7.3 to 7.5) at any of the dosages applied. The XAD-8 fraction also did not show significant dose effects for the 1:1 and 3:1 ozone:NVDOC ratios employed to generate the data shown in Figure

7.5. (Indeed, although not necessarily statistically significant, it appears that very high ozone dosages (greater than 1:1) may even increase THMFP.) However, if one also considers THMFPs from non-ozonated XAD-8 fractions (Figures 7.3 and 7.4), then it can be surmised that the optimum ozone dosage for THM precursor reduction must be less than 1:1 ozone:NVDOC for this fraction.

THMFPs determined from natural water chlorination displayed pH, alkalinity and ozone dosage effects which were consistent with those described above. The data are presented in Appendix VI. They confirm that an applied ozone:NVDOC ratio of less than 1:1 ozone:NVDOC may be optimum in reducing THM formation in the river water, but that further reductions are achievable in lakewater if dosages higher than 1:1 are employed. At these ozone dosages, THM reductions of 40 to 50 % were achievable for both sources. Considering that ozonation had little effect on the THMFP of XAD-4 isolated NOM, but approximately 50 % reductions were obtained for XAD-8 derived NOM, it may be that the major ozone treatable THM precursors in both of the raw water sources studied are similar in character to those isolated on XAD-8 resin (which are more aromatic).

The haloacetic acids (HAAs) are a group of chlorination DBPs which have recently received much attention due to ascribed toxicological properties (Chapter 1). Their formation potentials characteristics are different than those observed for the THMFPs. The results obtained for HAAFPs determinations in this research are shown in Figures 7.6 to 7.8. pH effects observed for HAAFPs were consistent with published data (Coleman *et al.*, 1992; Reckhow and Singer, 1984) in that greater yields were obtained at pH 6 than at pH 8. In addition alkalinity generally had little effect.

Observed pH effects on non-ozonated NOM were minimal for all fractions examined, except for lakewater NOM isolated on XAD-8. Clearly, ozone produced HAA precursors, particularly with river water NOM.

Alkalinity effects were not significant, with the exception of those observed for ozonated river water NOM fractions (Figure 7.7). Higher HAAFPs resulted with both

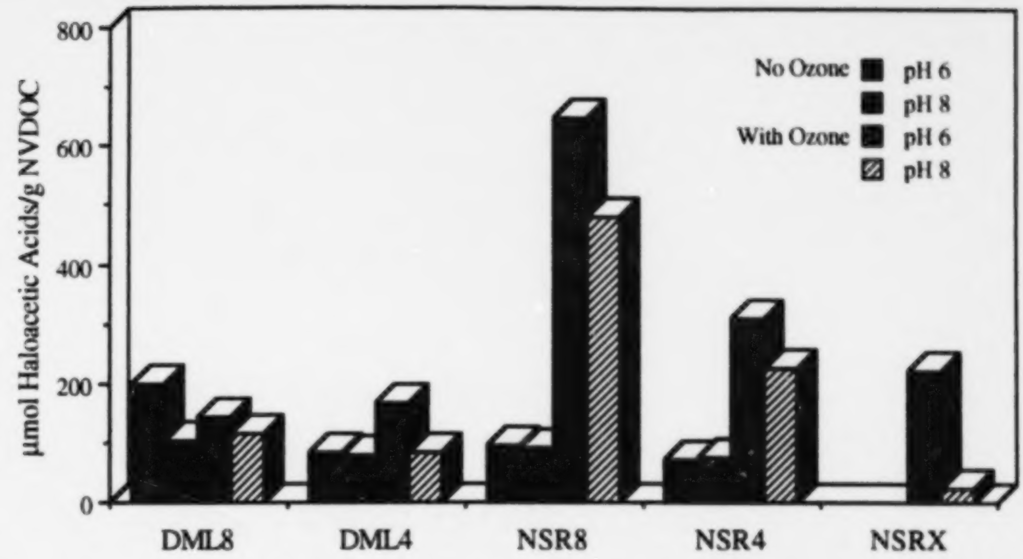


Figure 7.6 Effect of pH on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

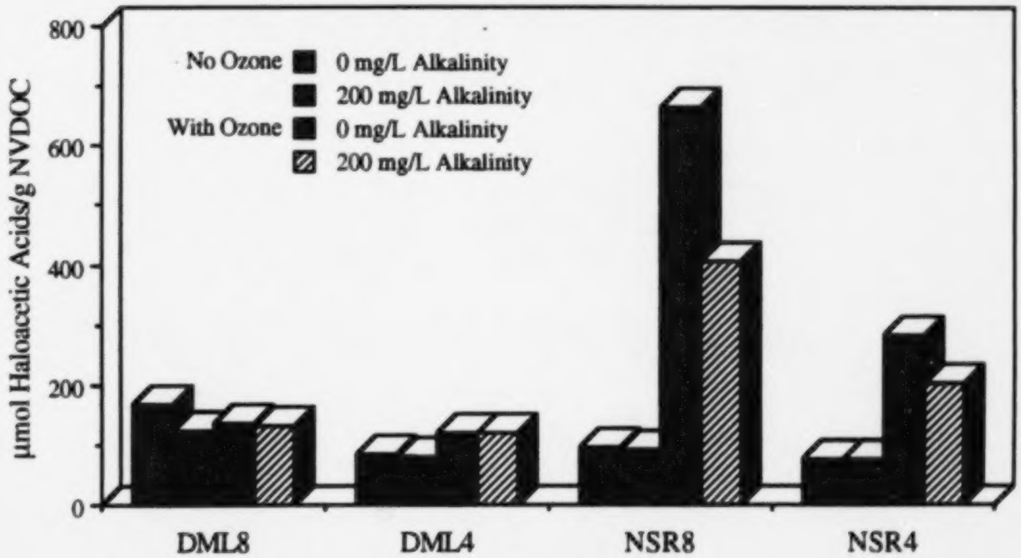


Figure 7.7 Effect of Alkalinity on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and ozone dose))

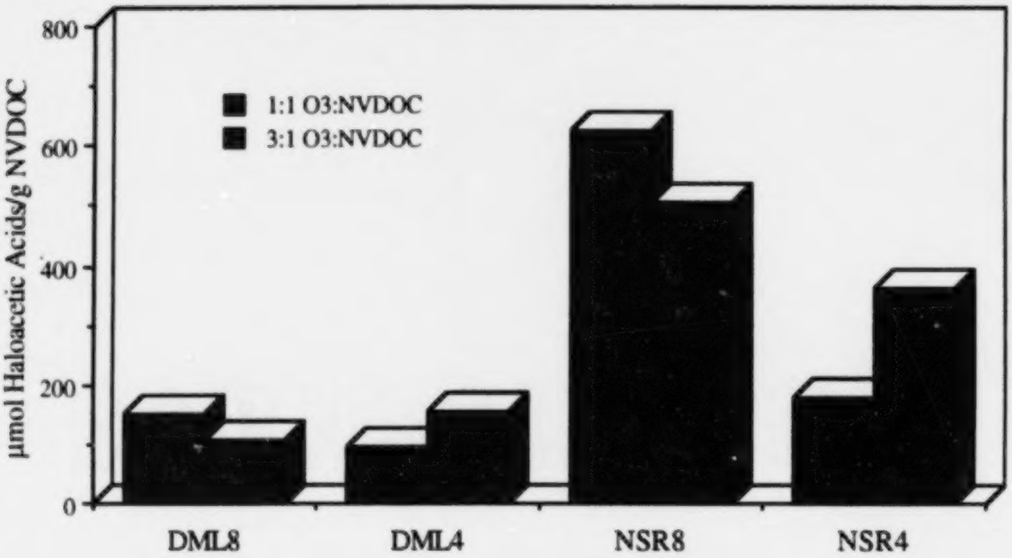


Figure 7.8 Effect of Ozone Dose on the Formation of Haloacetic Acids from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

XAD-8 and XAD-4 river water NOM fractions which were ozonated and then chlorinated without added alkalinity. These effects are likely due to the ozonation portion of the ozone-chlorine disinfection combination because alkalinity effects for non-ozonated NOM were insignificant. The observations imply that ozonation at low alkalinity produces more HAA precursors than at high alkalinity for river water NOM. Low alkalinity would favour at least some participation of radical reaction mechanisms.

For river water fulvic acid fractions, ozonation at the dosages employed increased HAAFPs by 300 to 600 % (Figures 7.6 and 7.7), whereas HAA precursors in lakewater NOM were less affected by ozone. Shown in Figure 7.8 are the effects of changing ozone dose from 1:1 to 3:1 ozone:NVDOC. The decrease in HAA for the XAD-8 fractions appears to contradict information presented in Figures 7.6 and 7.7. However, data in Figure 7.6 represent HAAFPs resulting from changes in ozone dose of 0:1 to an average of 2:1 ozone:NVDOC and data shown in Figure 7.8 are for ozone dose changes from 1:1 to 3:1 ozone:NVDOC. It may be that a plateau (or maximum) exists for HAA precursor formation somewhere below 3:1 ozone:NVDOC for the XAD-8 NOM fractions, but such a plateau (or maximum) may not exist for the HAA precursors resulting from XAD-4 fraction NOM ozonation within the range of ozone doses employed.

Similar pH, alkalinity and ozone dose effects were also observed for HAA production from the two natural water sources (Appendix VI). The results were generally similar to those obtained for the XAD-8 fractions. The apparent alkalinity effect observed for river NOM fractions was much reduced in the natural river water, as expected given the already high alkalinity present. Ozone dose effects were similar to those observed for the XAD-8 NOM fractions.

Chloral hydrate is an interesting XDBP in that it can be oxidized further to either trichloroacetic acid or chloroform (Stevens, *et al.*, 1990; Reckhow and Singer, 1986). Ozonation was shown to alter the magnitudes of the pH effects associated with chloral hydrate formation, and increased the overall yields regardless of NOM source (Figure 7.9).

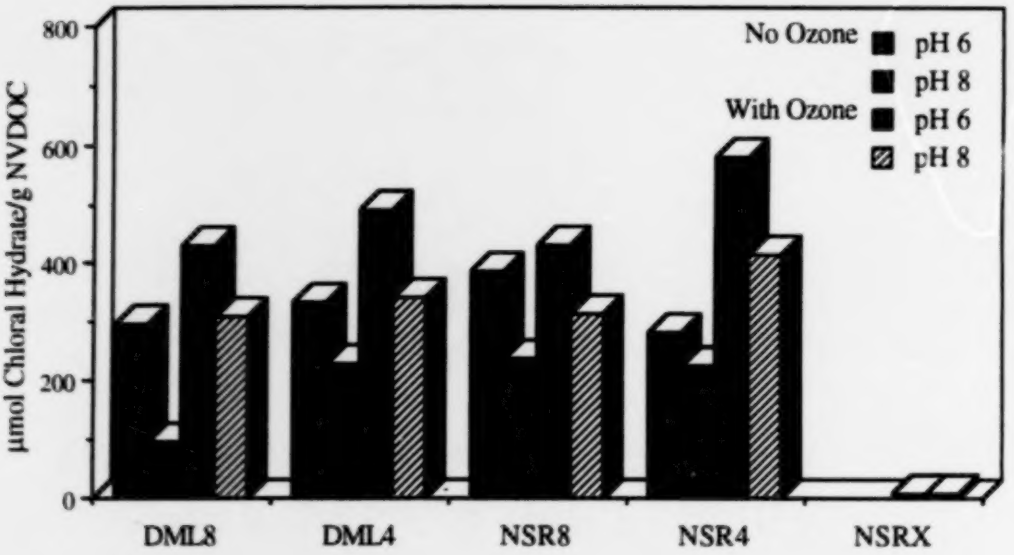


Figure 7.9 Effect of pH on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

Reduced pH effects were observed following ozonation of fulvic acids isolated on XAD-8 resin as evidenced by the smaller differences in average yield obtained at the two pH setpoints studied. Greater pH effects were observed for the NOM isolated on XAD-4 resin.

Chloral hydrate yields were higher for samples at pH 6 than at pH 8 (Figure 7.9). This observation was consistent among all samples and with data reported in the literature. Initial chloral hydrate formation typically occurs faster under basic conditions; however, chloral hydrate also oxidizes to chloroform and trichloroacetic acid under the same conditions. These competing reactions require that the interpretation of chloral hydrate yield data give some consideration to the reaction time involved. Stevens *et al.* (1990) reported that chloral hydrate decomposition rates significantly exceeded formation rates at a point between 4 and 48 hours of reaction, at pH 9.4. The long reaction times employed in the present research (7 days) would explain the relatively lower concentrations of chloral hydrate observed at pH 8 than at pH 6. Also, in comparing Stevens *et al.* (1990) data with those presented herein, it would appear that less hydrolysis occurred in the present research at pH 8 than in the former research at pH 9.4, indicating that the hydrolysis rate probably increases substantially between the two pH values. This may have important implications with regard to the stability of chloral hydrate in distribution systems in that even small pH differences between pH 8 and 9.4 could result in substantial differences in the distribution of the XDBPs chloral hydrate, trichloroacetic acid and chloroform seen at the tap. The competition of formation and hydrolysis reactions makes predicting formation of chloral hydrate concentrations difficult.

This complexity is also evident when comparing the chloral hydrate data obtained for NOM fractions to that for raw waters (Appendix VI). Contrary to what was observed for the isolated fulvic acids, chloral hydrate formation in lakewater exhibited no pH effects, and greater chloral hydrate formation was observed at pH 8 than at pH 6 in river water.

Alkalinity effects were not generally significant in chloral hydrate formation (Figure 7.10), although some instances of decreased chloral hydrate formation at higher alkalinity were noted even for raw water (Appendix VI). These alkalinity effects were not likely imposed during ozonation as non-ozonated water also showed them.

Increasing the ozone dosage from 1:1 to 3:1 ozone:NVDOC did not appear to increase chloral hydrate yields from NOM fractions substantially, as is shown in Figure 7.11 although slight increases were observed for lakewater NOM. This observation on its own would imply that ozone does not affect either formation or reduction of chloral hydrate precursors in river water NOM. However, in examining the data shown in Figure 7.9 which compares chloral hydrate yields obtained either without ozone or for which the mean ozone dose employed was 2:1 ozone:NVDOC, it is apparent that higher chloral hydrate yields were obtained on ozonation. Since chloral hydrate yields obtained at an ozone dosage of 2:1 were higher than those obtained without ozonation, and since mean results obtained at the 2:1 dose are not significantly different from those at 1:1 or 3:1, then similar to that summarized for THM formation, an ozone dose of less than 1:1 ozone:NVDOC appears optimal in producing chloral hydrate precursors from these NOM fractions. Ozone dose effects for natural waters were similar to those observed for fulvic acids isolated from river water, emphasizing the complex nature of the reactions in which chloral hydrate may be involved.

Chloral hydrate yields from XAD-4-isolated fulvic acids were typically greater than those from XAD-8-isolated NOM (Figure 7.9). The XAD-4 fulvic acids contain more chloral hydrate precursors per mass of material than do the XAD-8 fulvic acids. It is also apparent from the data in Figure 7.9 that the hydrophilic base fraction does not contain appreciable chloral hydrate precursors, at least not after ozonation and not when compared to the fulvic acids fractions.

Cyanogen chloride was rarely detected in chlorinated fulvic acid solutions or river water samples and so the data are not shown. However, it was formed in small amounts in

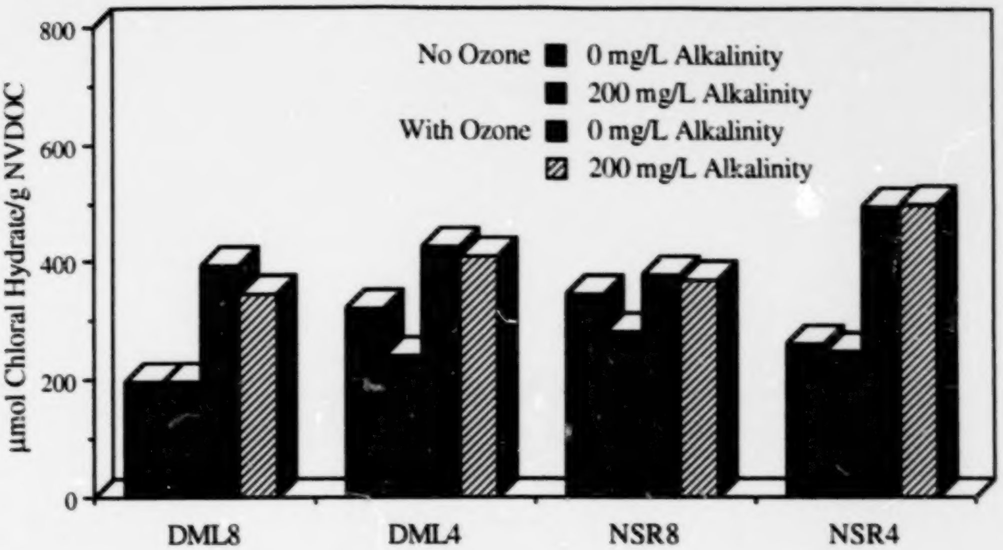


Figure 7.10 Effect of Alkalinity on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and dose))

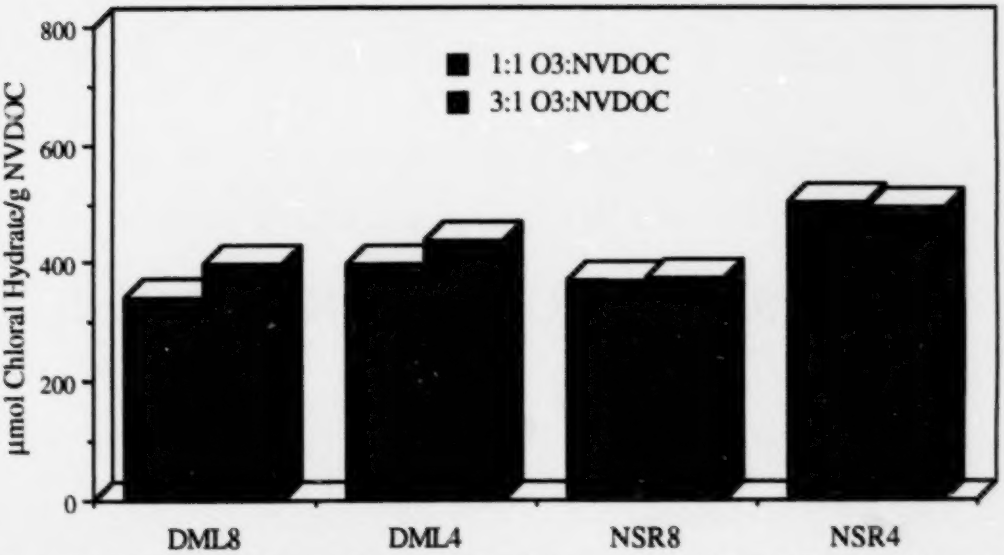


Figure 7.11 Effect of Ozone Dose on the Formation of Chloral Hydrate from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

lakewater samples and the data are presented in Appendix VI. Because of the small number of samples showing detectable levels of cyanogen chloride, the effects of the various ozonation-chlorination parameters employed are not discussed here but are included in Section 7.2.2 which presents the results obtained on chloramination.

7.2 Post-Ozone Chloramination

Chloramine is gaining popularity as an alternative disinfectant to chlorine because it decays more slowly than chlorine and does not produce the same magnitude of undesirable DBPs as those associated with chlorine. Chloramine hydrolyzes relatively slowly and therefore is present in effective concentrations for relatively long periods of time, making it appealing for maintaining a distribution system disinfectant residual. Because it is also a weaker oxidant than is chlorine, it produces chlorinated DBPs in lesser quantities. However, because of the long reaction times encountered in distribution systems, halogenated disinfection by-product (XDBP) formation resulting from chloramination cannot be ignored.

7.2.1 Effects of Ozonation Parameters on Oxidant Demand

For chloraminated samples, there were few discernable differences between the oxidant demands of the XAD-4 and XAD-8 isolates, regardless of source water therefore results are not shown. However the chloramine demands of the river NOM isolates were 20 to 30 % higher than those of the lakewater NOM. As was the case for the chlorinated samples, there were no alkalinity or ozone dosage effects noted. The effect of pH on chloramine demand varied, although the demand at pH 8 was generally 10 to 25 % less than that at pH 6. Experiments conducted using material chloraminated without ozonation showed this pH effect to be unrelated to ozonation and more probably due to speciation and hydrolysis of chloramine and subsequent reaction mechanisms at the two pHs evaluated.

7.2.2 Effects of Ozonation Parameters on XDBP Formation Potentials

Except for cyanogen chloride, all chloramination XDBPs were formed at lower concentrations than when chlorine was used. This is consistent with the literature. In order to avoid repeating much of the information already in the literature, some aspects of the formation of those XDBPs which are known to be reduced in concentration on chloramination will not be extensively discussed in this chapter but will be treated briefly. A more detailed discussion will be provided for cyanogen chloride formation, as it was the XDBP to show increased formation following chloramination.

The effects for trihalomethane formation potentials (THMFPs) resulting from chloramination were similar to those obtained on chlorination except that the THM yields were lower by approximately 50 to 80 %. Typical results, shown relative to results for chlorination, are illustrated in Figures 7.12 to 7.14 for lakewater NOM isolated on XAD-8 resin. THM formation was favoured at pH 8, although pH effects were not as great as those observed with chlorine, use of ozone reduced THMs formation. Similarly, alkalinity had no effect (Figure 7.13).

The effects on THMFPs obtained from chloramination of non-ozonated NOM fractions are shown in Figure 7.15 and were similar to those obtained for chloramination of natural water (Appendix VII). The effect of alkalinity on THMFP was negligible, as was determined for the chlorinated samples, but the effect of pH was the opposite to that observed on chlorination. Greater THM yields were observed at low pH than at high pH. Part of the reason for this lies in the pH dependence of the hydrolysis rates of chloramine, and the fact that free chlorine, not combined chlorine, participates in the haloform reaction. Therefore, chloramine must first hydrolyze to chlorine and ammonia before its chlorine component will react with THM precursors to form THMs, and the hydrolysis proceeds faster at pH 6 than at pH 8. A reason for this is that the dissociation of chloramine would be expected to be at a minimum between the two pKa's of its constituents (hypochlorous acid and ammonia at 7.5 and 9.3, respectively). Each of the fractions produced similar

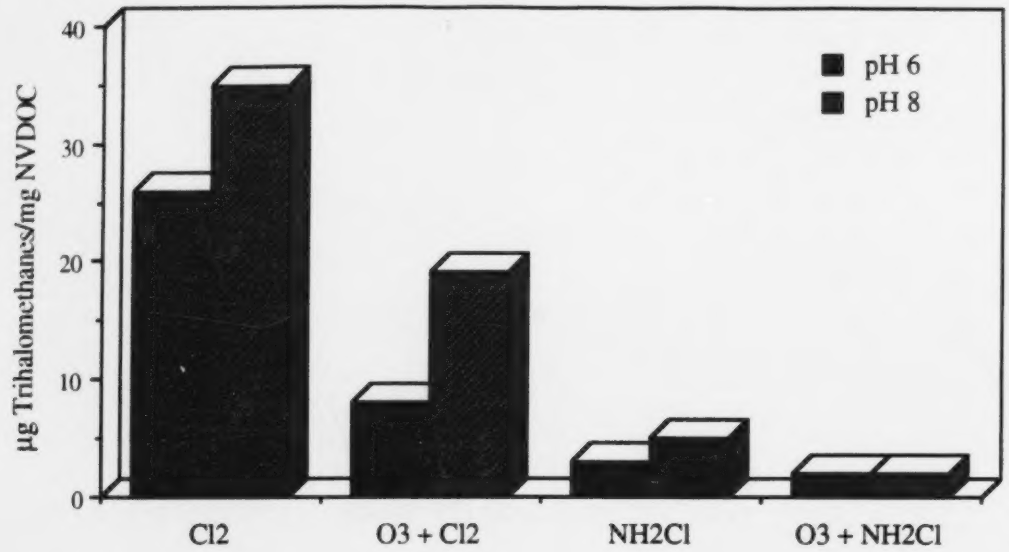


Figure 7.12 Effect of pH and Type of Oxidant used on THMFP (5 mg/L NVDOC, lakewater fulvic acids isolated on XAD-8 resin; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose)).

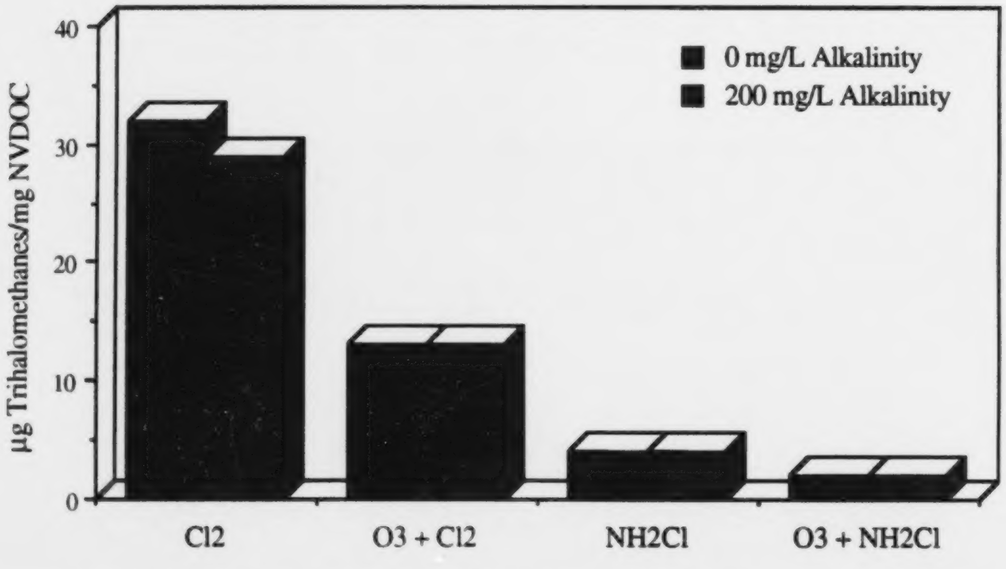


Figure 7.13 Effect of Alkalinity and Type of Oxidant used on THMFP (5 mg/L NVDOC, lakewater fulvic acids isolated on XAD-8 resin; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and dose)).

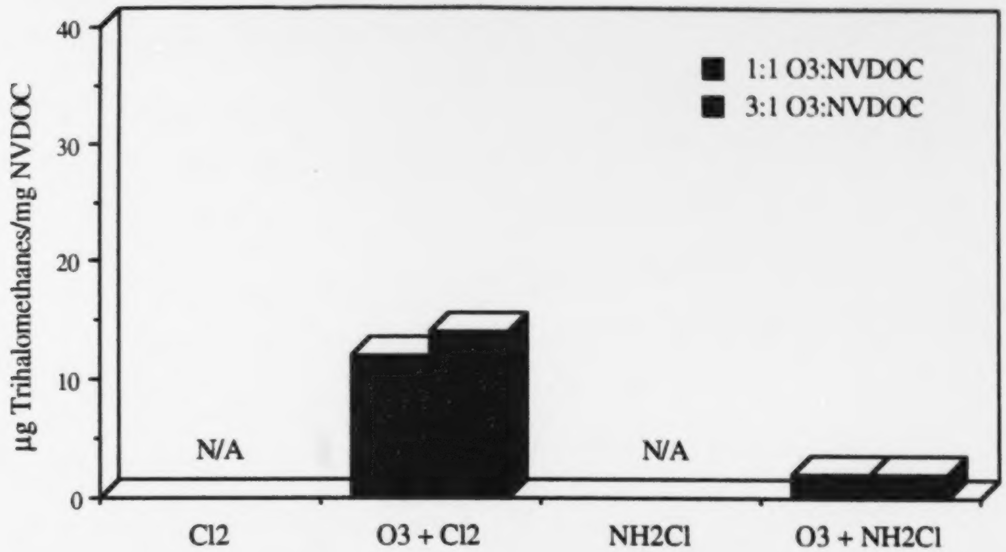


Figure 7.14 Effect of Ozone Dose and Type of Oxidant used on THMFP (5 mg/L NVDOC, lakewater fulvic acids isolated on XAD-8 resin, N/A = not applicable; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

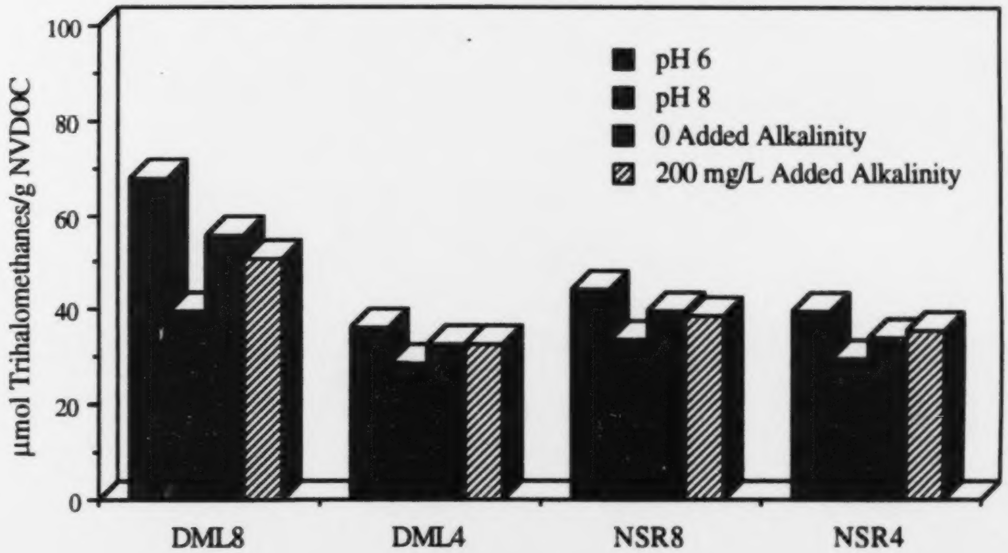


Figure 7.15 Effect of pH and Alkalinity on THMFP of Non-Ozonated NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8=XAD-8, 4=XAD-4; Because of the factorial design employed, the results plotted for each of the two levels of a given parameter (*e.g.* pH 6 and 8) include equal numbers of measurements made at both upper and lower levels of the other parameter (alkalinity))

amounts of THMs, except that the lakewater NOM isolated on XAD-8 produced slightly greater yields.

Haloacetic acid formation potentials (HAAFPs) followed a similar pattern to those of the trihalomethanes with regard to the relative effects of ozonation and chlorine or chloramines use, as shown in Figure 7.16 in that both ozone and chloramines resulted in decreased yields compared to data using chlorine. The pH effects were the same as those observed for chlorine usage (Figure 7.6) in that greater formation occurred at pH 6, and ozone acted to reduce HAA precursors even on chloramination. Alkalinity effects were observed to be minimal (Appendix VII).

Results for chloral hydrate were similar for both chlorination and chloramination, except as expected, the XDBP yields were considerably less following chloramination. Greater chloral hydrate yields were observed at pH 6 than pH 8 (Figure 7.17). This may have been due to hydrolysis of chloral hydrate at the higher pH value and the long reaction time employed in the formation potential test, as was discussed in the previous section for chlorination. Other effects were similar to those observed on chlorination and are illustrated in Appendix VII.

Greater chloral hydrate yields were associated with the fulvic acid fractions isolated from lakewater than from river water. The fact that few differences were noted between the two types of fractions obtained (XAD-8 *vs* XAD-4) may indicate that it was the aliphatic portion of the fulvic acids (common to both fractions) that was the source of the chloral hydrate precursors.

Cyanogen chloride (CNCl) was the only XDBP to be formed in greater yield following chloramination when compared to chlorination. As shown in Figures 7.18 to 7.20, ozone enhanced CNCl formation for lakewater NOM fractions but appeared to reduce formation of CNCl from river water NOM. Even chlorine alone produced CNCl above detection limits for lakewater NOM but not river water fractions (shown in Appendix VII), likely because of the higher nitrogen content of the lakewater fulvic acids. CNCl

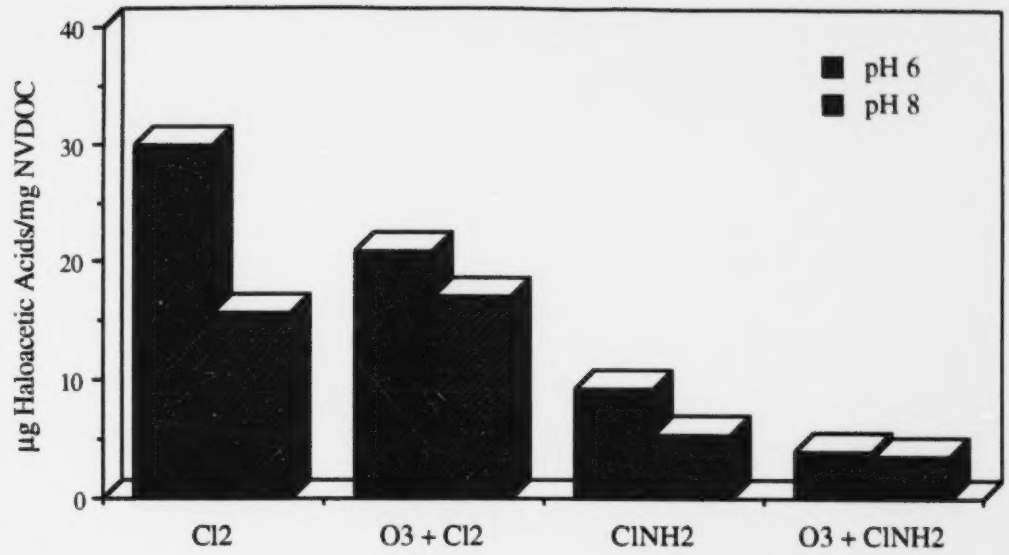


Figure 7.16 Effect of pH and Type of Oxidant used on HAAFP (5 mg/L NVDOC, lakewater fulvic acids isolated on XAD-8 resin; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

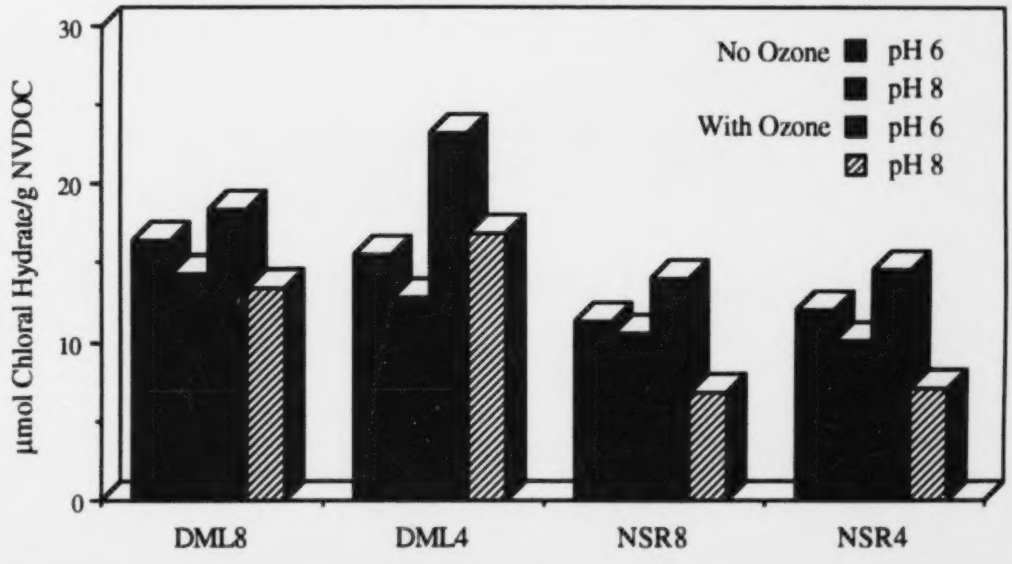


Figure 7.17 Effect of Ozone Dose and Type of Oxidant used on CHFP (2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

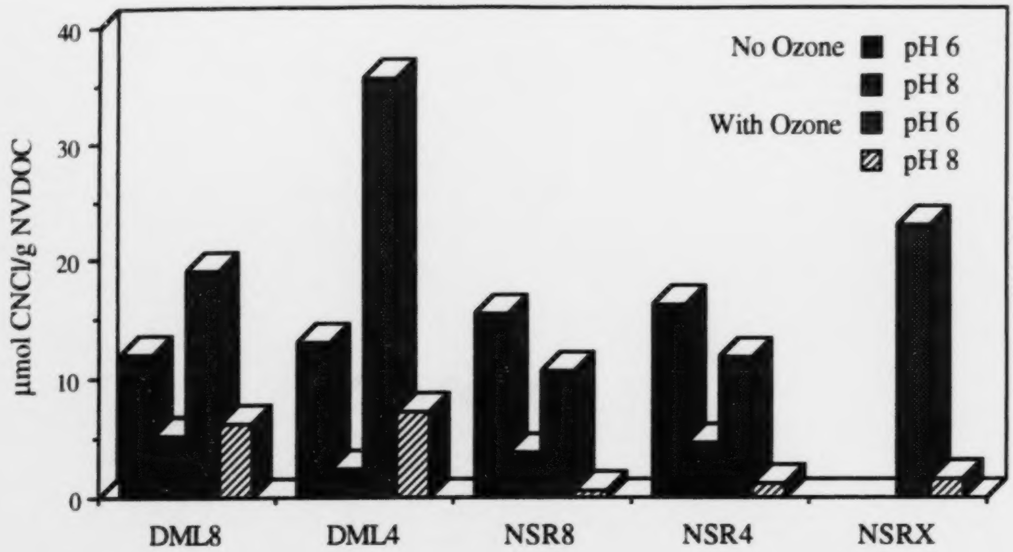


Figure 7.18 Effect of pH on the Formation of Cyanogen Chloride from the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4, X = AG MP-50; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

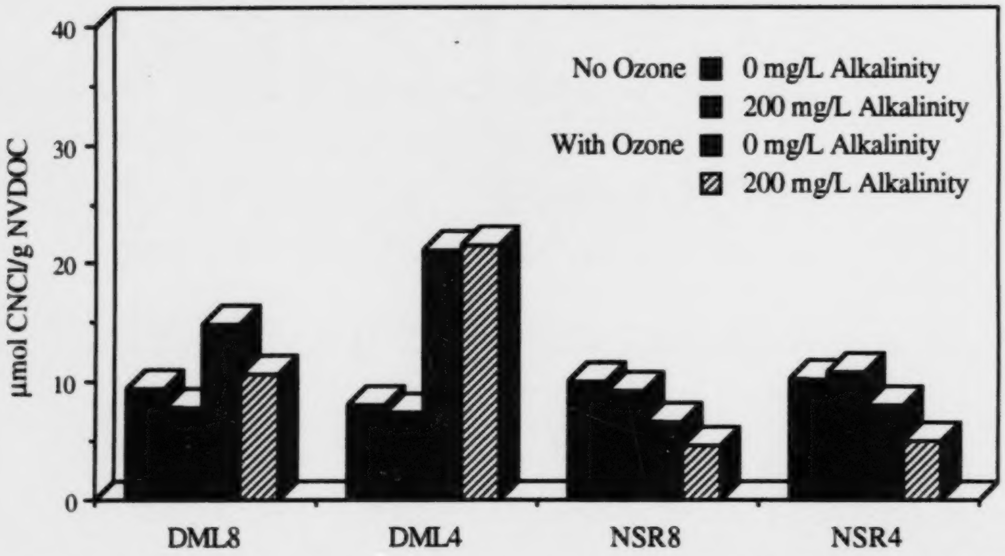


Figure 7.19 Effect of Alkalinity on the Formation of Cyanogen Chloride Following the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River 8 = XAD-8, 4 = XAD-4; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two alkalinity levels include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and dose))

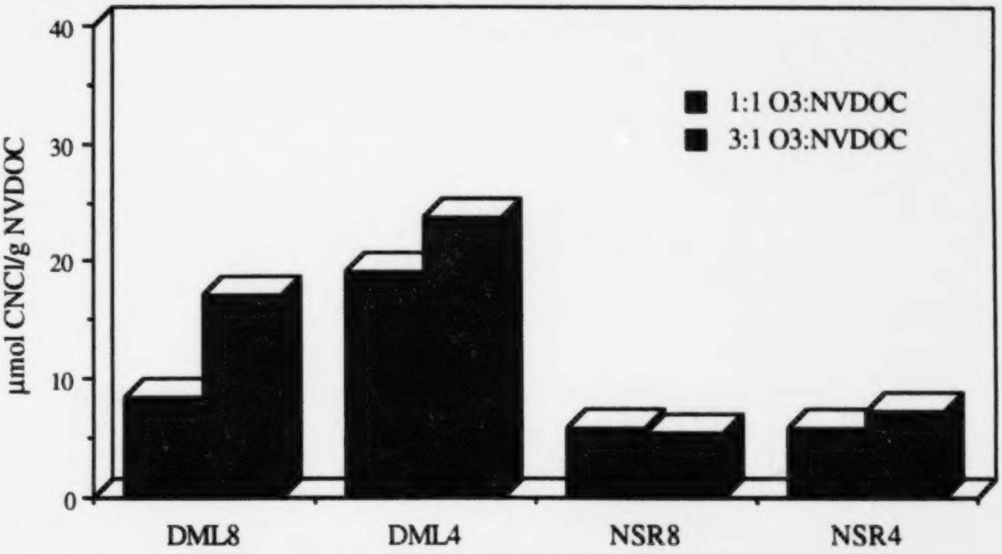
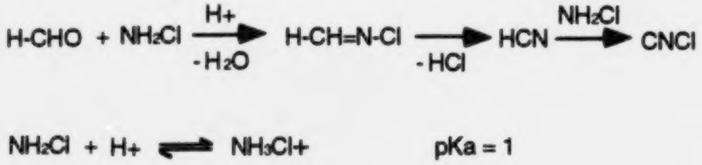


Figure 7.20 Effect of Applied Ozone Dosage on the Formation of Cyanogen Chloride Following the Ozonation of NOM Fractions (DML = Driedmeat Lake, NSR = North Saskatchewan River, 8 = XAD-8, 4 = XAD-4; Because of the factorial design employed, the results plotted for each of the two ozone doses include equal numbers of measurements made at both upper and lower levels of the other parameters (pH and alkalinity))

production on chlorination alone, and its enhanced production on chloramination (especially when pre-ozonation is employed), have also been observed by Krasner *et al.* (1991).

Cyanogen chloride formation potentials (CNClFPs) were measured before and after ozonation, under varying conditions of pH, alkalinity and ozone dose. The most pronounced effect on CNCl formation was pH, whereby formation at pH 6 was without exception much greater than that at pH 8 (Figure 7.18). Scully (1990) postulated that CNCl could be formed from formaldehyde (increased in concentration on ozonation) and chloramine at low pH, possibly involving a NH_3Cl^+ species, as shown below.



$$\text{H-CHO} + NH_2Cl \xrightarrow[-H_2O]{H+} \text{H-CH=N-Cl} \xrightarrow[-HCl]{} HCN \xrightarrow{NH_2Cl} CNCl$$

$$NH_2Cl + H+ \rightleftharpoons NH_3Cl+ \qquad pKa = 1$$

Xie and Reckhow (1992b) reported that CNCl decomposed rapidly at pH greater than 9, and possibly also at a pH as low as 8, which could account for low CNCl yields at high pH. Although lakewater NOM, especially that isolated on XAD-4, showed that CNCl formation increased following ozonation, river water NOM exhibited the opposite effect. Ozonation of hydrophilic bases also produced CNCl precursors. Data for non-ozonated hydrophilic bases were not available.

Alkalinity had a much smaller effect on CNCl production than did pH (Figure 7.19). For non-ozonated NOM, alkalinity had little to no effect. Upon ozonation, high alkalinity resulted in lower post-chloramination CNCl yields for most NOM fractions, indicating that some CNCl precursors might be formed *via* radical reactions with the NOM.

Higher ozone doses produced greater amounts of CNCl precursors from lakewater NOM, but not from river water NOM (Figure 7.20). In comparing Figures 7.18 and 7.20, these results are corroborated for the lakewater NOM. For river water NOM, it is shown in Figure 7.18 that CNCl precursors decreased on ozonation.

The pH effects of formation of CNCl in natural water matrices are shown in Figure 7.21. Alkalinity and ozone dose effects are illustrated in Appendix VII. pH effects agreed with those observed for the isolated NOM fractions: greater yields were obtained at pH 6 than at pH 8. The effects of ozone dose on CNCl formation from lakewater shown in Figure 7.21 agrees with that observed for corresponding NOM fractions whereas those for river water appear to contradict the information presented for the NOM fractions (Figures 7.18 to 7.20). For river water Figures 7.18 and 7.19 show a slight decrease in CNCl yield on changing from 0 to an average of 2:1 ozone:NVDOC, whereas Figure 7.20 shows no effect (1:1 to 3:1 ozone:NVDOC) and Figure 7.21 indicated a marked increase in CNCl yield on ozonation. There may have been substances present in river water which were not isolated by XAD resin adsorption, and which, upon ozonation, became precursors for CNCl. This unidentified material could account for a significant portion of the yield of CNCl from the ozonated natural water matrix. It is also possible that the fulvic acid extraction procedure simply modified the CNCl precursor material and caused the observed decrease in CNCl production.

7.3 Summary

The various results for formation of XDBPs from chlorination and chloramination of selected fulvic acids and natural waters in this research agree in general with data reported in the literature, including effects of ozonation prior to chlorination or chloramination. However specific aspects describing the effects of pH, alkalinity and ozone:NVDOC ratio are reported in the following.

pH was the parameter shown to have the greatest effect on XDBP formation. the pH effects observed were consistent with known reaction mechanisms. Alkalinity effects

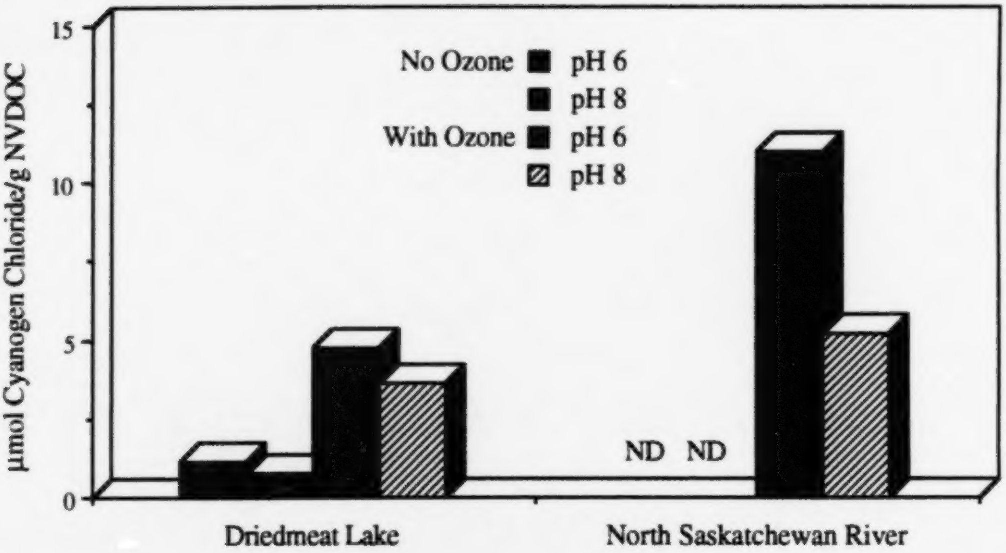


Figure 7.21 Effect of pH and Ozone on the Formation of Cyanogen Chloride in Natural Water Matrices (NVDOC: 16.35 mgC/L lakewater, 1.67 mgC/L river water; 2:1 O_3:NVDOC; Because of the factorial design employed, the results plotted for each of the two pH levels include equal numbers of measurements made at both upper and lower levels of the other parameters (alkalinity and dose))

were negligible, except as they related to the results of ozonation experiments in which alkalinity affected precursor production.

Ozone dose effects between 1:1 and 3:1 applied ozone:NVDOC ratios were minimal except for cyanogen chloride formation. Careful examination of the data revealed that optimum precursor formation must occur at an ozone dose of less than 1:1, or for some XDBPs between 1:1 and 2:1 applied ozone:NVDOC.

The chlorine demand experienced by each fraction was different. The hydrophilic bases exerted the greatest chlorine demand of all of the fractions when the tests were performed at pH 6. This has been attributed to N-organochlorine formation as this fraction contained a high nitrogen content, likely largely in the amino form due to the isolation procedure used. Of the fulvic acid fractions, those isolated on XAD-4 resin exerted approximately twice the chlorine demand as did those isolated on XAD-8. This may have been partly due to the differences in their respective molecular weights as the results are expressed on a per gram basis.

Chloramines produced smaller quantities of most XDBPs than did chlorine, the exception being cyanogen chloride, as reported in the literature.

Analyte decomposition or hydrolysis complicated interpretation of some of the results, particularly for chloral hydrate and cyanogen chloride. Had different chlorination or chloramination times been employed in the formation potential tests, competition between XDBP formation and decomposition may have resulted in reaction parameter effects being different from those measured in this research.

CHAPTER 8

CONCLUSIONS

8.1 Precursor Concentration Effects

The data presented in this research illustrated and emphasized the problem of extrapolating bench scale data (often obtained at higher than ambient reactant concentrations) to real situations. In consideration of these findings, if such data are extrapolated to NVDOC (non-volatile dissolved organic carbon) concentrations lower than those on which the database was formed, both the extent of colour reduction (as measured by UV absorbance) and disinfection by-product (DBP) formation can be seriously underestimated. When compared to each other, relative yields of the individual DBP classes differed at the two concentrations employed. Concentrations of aldehydes (relative to the NVDOC concentration) formed at low NVDOC concentrations were much greater than the other classes of DBPs when compared with results obtained at the higher NOM concentration. It has long been recognized that DBP formation cannot be predicted globally, *i.e.* for several source water types from data not obtained at those sites, due to differences in source water characteristics. The data presented herein show that even if such data are available for a given site, it may be difficult to predict DBP formation for that site under varying NVDOC concentrations.

8.2 Effects of Ozonation Parameters on Colour and DBPs

Studies of organic DBP production from the ozonation of the isolated NOM fractions yielded the following information. At concentrations of either 5 or 20 mg/L NVDOC, it was apparent that the fulvic acids reacted both as radical scavengers and promoters, and that the transition between the two states might lie between ozone:NVDOC dosage ratios of 1:1 and 3:1 ozone:NVDOC. When considering organic by-products of ozonation, pH was the parameter having the greatest influence on DBP yields, and greater yields of aldehydes and carboxylic acids were obtained at pH 6 than at pH 8. The influence of pH on the formation of oxoacids and UV absorbance reduction was different than for aldehydes and carboxylic acids, possibly because of participation in different reaction mechanisms (molecular *vs* radical). UV reduction did not correlate well with oxoacid production at the higher NVDOC concentration, but correlated well at the lower NVDOC concentration, possibly because the interactive effects of pH and alkalinity were more pronounced at the higher NVDOC concentration.

The different NOM fractions contributed differently to the DBP yields. For example, the XAD-4 isolated fulvic acids produced greater quantities of aldehydes and oxoacids than did the XAD-8 fractions. The hydrophilic base fraction contributed significantly to the formation of aldehydes and oxoacids but produced few carboxylic acids and was not significantly involved in overall UV absorbance reduction. Also, DBP formation characteristics were somewhat site specific in that lakewater ozonation produced higher levels of carboxylic acids whereas ozonation of river water fulvic acid from the International Humic Substances Society (IHSS) produced greater quantities of aldehydes.

The observed increases in DBP yields with increases in fulvic acid concentration implied that all of the DBPs studied could be considered to be precursors of free radical reactions. This might be especially true for one oxoacid, ketomalonic acid, which was different from the other DBPs in that its production increased much more dramatically with increasing NVDOC concentration. The observations regarding this oxoacid also lend support to a hypothesized reaction mechanism for its formation from quinone-type precursors in fulvic acid macromolecules.

The interactive effects between the ozonation variables pH and alkalinity were studied at the higher NVDOC concentration. Maximum aldehyde formation was observed at minimum pH and maximum alkalinity, whereas oxoacids were formed in greater quantities at high pH and alkalinity. At the lower ozone dose (1:1 ozone:NVDOC), there was an apparent minimum with respect to aldehyde formation and pH-alkalinity interactions were almost a non-effect. The interaction and synergistic effects of pH and alkalinity were most pronounced at the higher ozone dosage examined (3:1 ozone:NVDOC mass ratio).

While qualitatively similar results were observed for the ozonation of natural waters, the relative yields of some DBPs differed from those obtained in experiments employing isolated fulvic acid fractions. This was particularly true for the carboxylic acids and aldehydes, indicating that precursors other than fulvic acids were present in the natural water samples. In contrast, the yields of oxoacids were similar in both simulated and natural waters, indicating that components of the fulvic acids may constitute the major precursor material for this class of DBPs.

Contained in the above are implications for future research considerations and water treatment practice. Because a greater proportion of NOM was included in these studies than has typically been reported, data contained herein may be better applied to the estimation of effects encountered under typical drinking water treatment conditions than has previously been possible. As such, the data presented in this research may also help resolve contradictions in the literature, or at least provide some framework for which the data may be reinterpreted.

8.3 Effect of Ozonation on Chlorine Demand and XDBP Production

In this research, observations concerning halogenated DBP (XDBP) formation from chlorination and chloramination of selected fulvic acids and natural waters generally agreed with data reported in the literature, including inferences with respect to the effects of ozonation prior to chlorination or chloramination. pH was shown to be the parameter having the greatest effect on XDBP formation. Observed pH effects were consistent with known reaction mechanisms. Alkalinity effects were negligible, except as they related to the results of ozonation experiments in which alkalinity affected precursor production. Ozone dose effects between 1:1 and 3:1 applied ozone:NVDOC ratios were minimal except for cyanogen chloride formation. Careful examination of the data revealed that optimum precursor formation for the majority of the XDBPs studied must occur at an ozone dose of less than 1:1 ozone:NVDOC. For some XDBPs an applied ozone dose of between 1:1 and 2:1 applied ozone:NVDOC was required. In general, chloramines produced smaller quantities of most XDBPs than did chlorine. An exception was cyanogen chloride, as has also been reported in the literature, especially that formed from the XAD-4 and hydrophilic base NOM fractions..

Different fractions of isolated natural organic matter exerted different chlorine demands. Of the fractions tested, the hydrophilic bases exerted the greatest chlorine demand when the tests were performed at pH 6. This was postulated to be attributed to N-organochlorine formation as this fraction contained a high nitrogen content, likely largely in the amino form due to the isolation procedure used. Of the fulvic acid fractions, those isolated on XAD-4 resin exerted approximately twice the chlorine demand as did those isolated on XAD-8. This may have been partly due to the differences in their respective molecular weights as the results are expressed on a per gram basis (Section 7.1.1).

Analyte decomposition or hydrolysis complicated interpretation of some of the results, particularly for chloral hydrate and cyanogen chloride. Interpretation of the yields of related DBPs depended on considerations of reaction times employed, since as the reaction proceeded their relative concentrations changed.

In addition to helping to resolve contradictions in the literature, or at least providing a framework for which the data may be reinterpreted, the results summarized above suggest possible future directions for drinking water research and water treatment practice. Including a greater proportion of NOM in investigations, as was applied in these studies, allows data obtained to be more readily applied to typical drinking water treatment conditions than has previously been possible. For example, the hydrophilic base fraction, not previously studied in this context, was shown to be a significant precursor material for cyanogen chloride formation, and was a major contributor to chorine demand. Conditions to minimize this and other XDBPs can be inferred from the results of this research.

8.4 Effectiveness of NOM Isolation Procedures

The natural organic matter (NOM) isolation procedure performed in this research was observed to proceed in a similar manner to that employed by others. Chromatographic effects were qualitatively similar to those reported by Malcolm (1991), although the resin capacity greatly exceeded expectations, and comparisons of adsorption monitoring data obtained during isolation of the hydrophilic base fraction compared well with that described by Leenheer (1981). Yields of NOM fractions were in agreement with calculations made based on NVDOC measurements and were similar to those obtained by others with similar NVDOC. As well, the relative characteristics and amounts of humic and fulvic acid obtained agreed with that published in the literature.

UV absorbance and NVDOC measurement methods were shown to be complementary for monitoring the adsorption process. NVDOC measurements sometimes detected non-humic interferences (methanol), while UV absorbance measurements were specific for the coloured humic material and were a better indicator of the adsorption of that component of NOM.

Chemical and spectral characteristics of the fulvic acids isolated on XAD-8 resin were similar to those for a corresponding "reference" grade material available from the IHSS. Some differences such as nitrogen content were attributed to source water type differences (eutrophic lake *vs* river). The XAD-8 and XAD-4 isolated fulvic acid fractions differed in their aromatic and aliphatic contents, carboxyl content and average molecular weight. The XAD-4 isolates were more aliphatic, had greater carboxyl content, but were of lower average molecular weight than were the XAD-8 isolates. Differences in specific UV absorbance measurements (expressed as absorbance/cm/g NVDOC) for the two fractions could not be solely ascribed to differences in molecular weight.

The hydrophilic bases were quite different from the fulvic acids, most notably in their highly aliphatic character, lack of colour and high nitrogen content. This was not unexpected, the ion exchange resin used can concentrate organic amines.

Inclusion of the XAD-4 and AG MP-50 fractions, both of which are relatively new, in studies involving NOM accounts for a significantly greater portion of the NOM pool. Their consideration adds significantly to the extrapolation of research results to natural water conditions when compared with making interpretations based on results obtained with XAD-8 fractions alone.

This research also shows that studies utilizing these new NOM fractions may help reconcile some of the contradicting results obtained previously, comparing results obtained using fractionated NOM with those of whole waters, because a greater portion of the NOM will have been included.

CHAPTER 9

RECOMMENDATIONS

9.1 Experimental Conditions

The following recommendations relate to the manner in which similar research involving natural organic matter (NOM) could be conducted and the results evaluated.

1. Of primary importance in predicting disinfection by-product (DBP) formation is consideration of concentration effects such as those described in this thesis. DBP production did not change in direct proportion with changes in precursor concentration, therefore extrapolation of bench scale data obtained at elevated concentrations to full scale situations can be misleading.
2. Consideration for individual DBP species should be made in DBP formation model formulations, especially since changes in precursor concentration did not effect the same type of change in normalized DBP yield. For example, aldehyde yields varied much more with NOM concentration than did concentrations of the other DBPs. In addition, ketomalonic acid yields increased with increasing fulvic acid concentration, whereas yields of other DBPs showed the opposite effect.
3. If DBP precursors are to be reliably investigated, NOM fractions such as those isolable on XAD-4 resin and AG MP-50 resin should be included because these fractions contribute significantly to the formation of many classes of DBPs.

9.2 Full Scale Drinking Water Treatment

Although the data reported in this thesis resulted from bench tests, the following recommendations with regard to their application at full scale may be made.

1. If colour reduction is the primary aim of the treatment process, then ozonation must be performed at some point in the treatment train where the pH is low but alkalinity

is high, and should employ ozone dosages of between 1:1 and 3:1 applied ozone:NVDOC. These conditions produced the greatest reduction in fulvic acid solution colour.

2. Removal of precursor material prior to ozonation remains the most important parameter in reducing DBP yields. The greatest observed changes in actual DBP yields, rather than yields normalized to NOM concentration, were a direct result of changing NOM concentrations, particularly for the aldehydes. However, because of the observed concentration effects there may be a practical limit to the viability of precursor reduction because increased efforts would not be cost-effective.
3. Since pH was also a factor in determining DBP yields, consideration should be given to the placement of ozonation units in a treatment plant to aid in reducing DBP formation. For example, aldehydes and carboxylic acids were formed in higher concentrations at low pH; therefore to reduce formation of these DBPs, an ozonation unit should be placed at a point in the treatment train which experiences relatively high pH.
4. Hydrophilic bases should be removed prior to chlorination or chloramination in order to reduce the chlorine demand of water in the distribution system and minimize cyanogen chloride formation. This fraction of NOM contributed significantly to the chlorine demand, likely by forming N-organochloramine species. N-organochloramines can be detected in water as being part of the disinfectant residual, however these species are not effective disinfectants. Therefore, in waters high in this NOM fraction, disinfectant residual measurements can be misleading and may result in inadequate disinfection in the distribution system by resulting in underdosages of effective disinfectant. In addition, this NOM fraction contributed significantly to cyanogen chloride formation, even when chlorine was the oxidant used, and the yields were greatly increased when ozone was employed prior to chlorination or chloramination.

9.3 Future Research

There were several aspects of NOM characterization and ozonation DBP production which became apparent during this research and which warrant further investigation. The following describes the most significant recommendations.

1. Because the NOM isolated on XAD-4 resin contributed significantly to DBP formation, more research should be done to determine means of reducing concentrations of these low molecular weight, aliphatic fulvic acids. Current treatment processes which may be considered for the study of removing these low molecular weight compounds include biological treatment, activated carbon adsorption, ion exchange and oxidation.
2. Similarly, it would be worthwhile to study the removal of hydrophilic bases. This fraction of NOM which was shown to contribute significantly to the formation cyanogen chloride and to increased chlorine demands, issues which are central in assessing drinking water distribution system stability and safety. Ion exchange or polymeric coagulant additives may be useful in effecting concentration reductions of these DBP precursors.
3. Quinone-type compounds should be further studied as possible precursors for some DBPs, particularly with reference to the formation of oxoacids.
4. There remains a lack of available analytical methodology for the determination of disinfection by-products, particularly with respect to polar DBPs expected to result from chemical disinfection of drinking water. Development of methods should be considered to improve detection of DBPs of current interest, and be expanded to include as yet unidentified DBPs. For example, DBPs possessing heteroatoms (nitrogen, sulfur, phosphorus) have not been considered in any detail with regard to drinking water treatment, yet compounds containing these elements participate in

metabolic processes and are ubiquitous. Identification of these DBPs would facilitate further study with respect to the toxicology of disinfection.

5. NOM isolation methods should be further developed to improve material fractionation which would enhance DBP precursor identification and removal efforts. Of particular interest would be the the isolation of the polar materials, not possible by existing methods.

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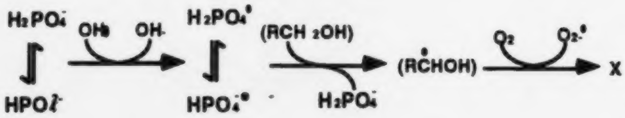
APPENDIX 1

ADDITIONAL QA/QC AND ANALYTICAL METHODS DEVELOPMENT INFORMATION

pH Buffer Considerations

Buffers are commonly used to control pH during chemical reactions, however they may actually participate in these reactions and affect their outcomes in many ways. Buffers were required to control the pH of the test solutions at pH 6, 6,3 and 8 ± 0.1 in the ozonation experiments performed for this thesis. Phosphate buffers were considered for the pH 6 setpoint. Initially, borate buffers were considered for pH 8 because the practical limit of phosphate buffers is near pH 8. However, initial tests showed that solutions of borate buffer could not be made to retain a detectable ozone or oxidant residual, and because of this scavenging ability the use of borate was abandoned.

Phosphate buffers at either pH 6 or pH 8 did not show any ozone scavenging ability. Staehelin and Hoigné (1985) showed that phosphate reacts with hydroxyl radicals generated from the decomposition of ozone as follows,regenerating the reactive $O_2^{\cdot -}$ radical



(I-1)

in the presence of organics and excess oxygen. (Borate was not tested.) This shows that phosphate is both a scavenger and promoter, and has no net effect on radical reactions.

However, with regard to the use of phosphate on subsequent chlorination or chloramination experiments, some research has indicated that phosphate can adversely affect halogenated disinfection by-product (XDBP) yields. Heasley *et al.* (1989) found that in the chlorination of resorcinol, only trace amounts of some intermediate XDBP species were detected when phosphate buffers were employed at high concentration (2 M). They postulated that phosphate anion attacked a cationic precursor to form a phosphate ester prior to aromatic ring opening which was not amenable to gas chromatographic analysis.

The data reported in this thesis should be comparable to the work of others, even though some intermediate XDBP species may not be detected, since phosphate buffers are commonly employed by others at the concentrations used herein.

Table I.1 Method Detection Limits* for Organic Ozonation Compounds

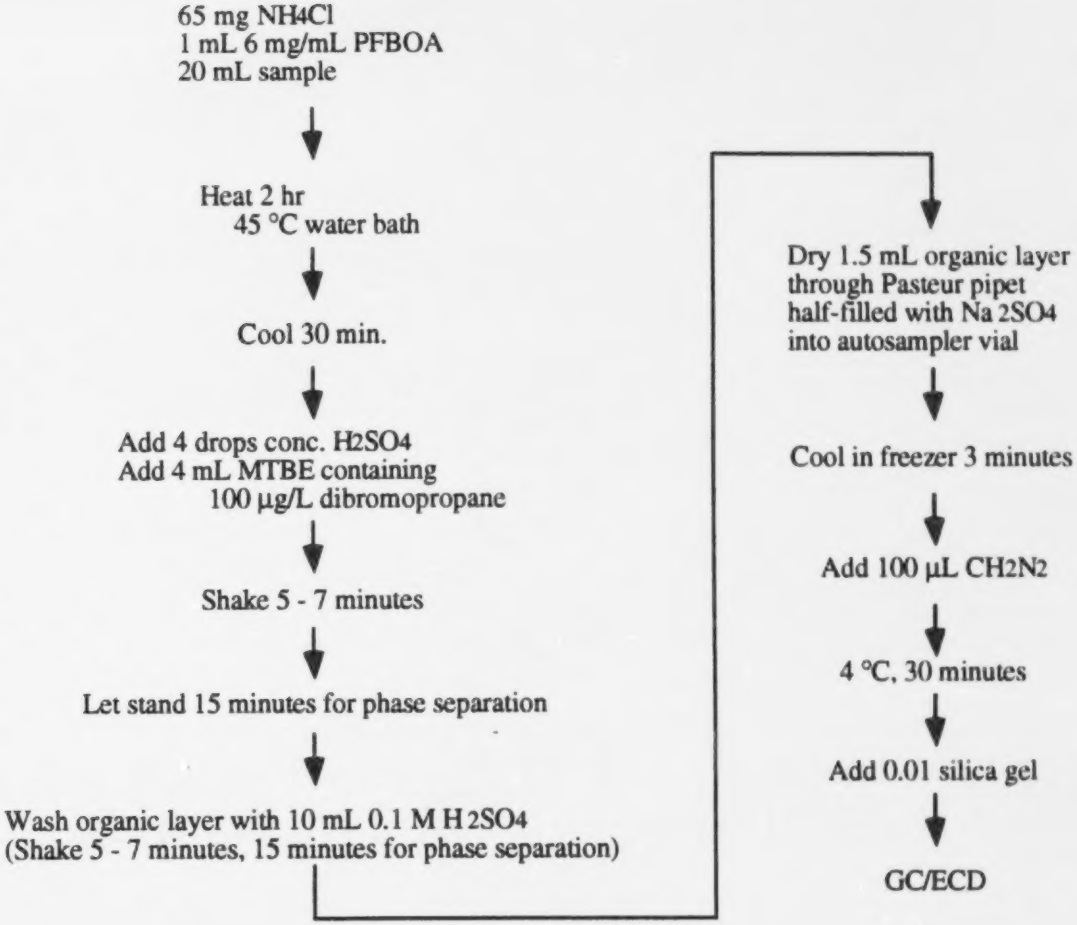
Class	Compound	Detection Limit (µg/L)
Aldehydes	Formaldehyde	0.45
	Acetaldehyde	1.23
	Glyoxal	0.62
	Methyl glyoxal	1.12
Oxoacids	Pyruvic acid	0.41
	Oxalacetic acid	0.77
	Glyoxalic acid	0.52
	Ketomalonic acid	0.57
Carboxylic Acids	Formic acid	8.13
	Acetic acid	7.55
	Propanoic acid	1.45
	Benzoic Acid	1.28

* Determined according to US-EPA protocols (3.0 times the standard deviation of seven replicates of solutions at concentrations near the detection limit).

Table I.2 Method Detection Limits* for the Halogenated Disinfection By-Products Studied

Analyte	Method Detection Limit (µg/L)
Chloroform	1.0
Dichlorobromomethane	0.2
Dibromochloromethane	0.2
Bromoform	0.2
Dichloroacetic acid	0.1
Trichloroacetic acid	0.2
Chloral hydrate	0.1
Cyanogen chloride	0.1

* Determined according to US-EPA protocols (3.0 times the standard deviation of seven replicates of solutions at concentrations near the detection limit).



GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 250 °C, detector 300 °C
oven: 100(5)-10-295(5)

Figure I.1 Outline of Method for the Analysis of Oxoacids

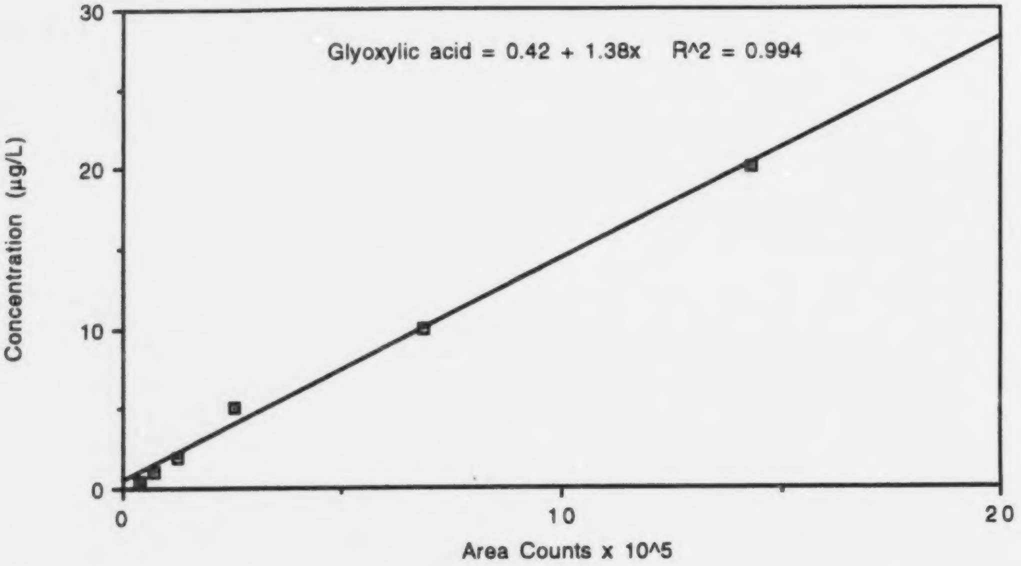


Figure I.2 Typical Calibration Curve for Glyoxylic Acid

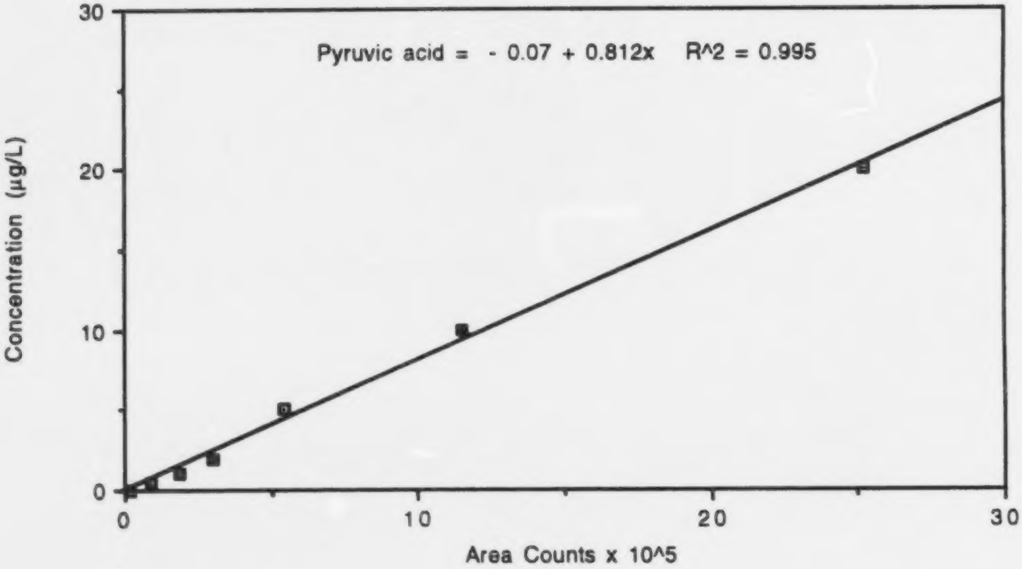


Figure I.3 Typical Calibration Curve for Pyruvic Acid

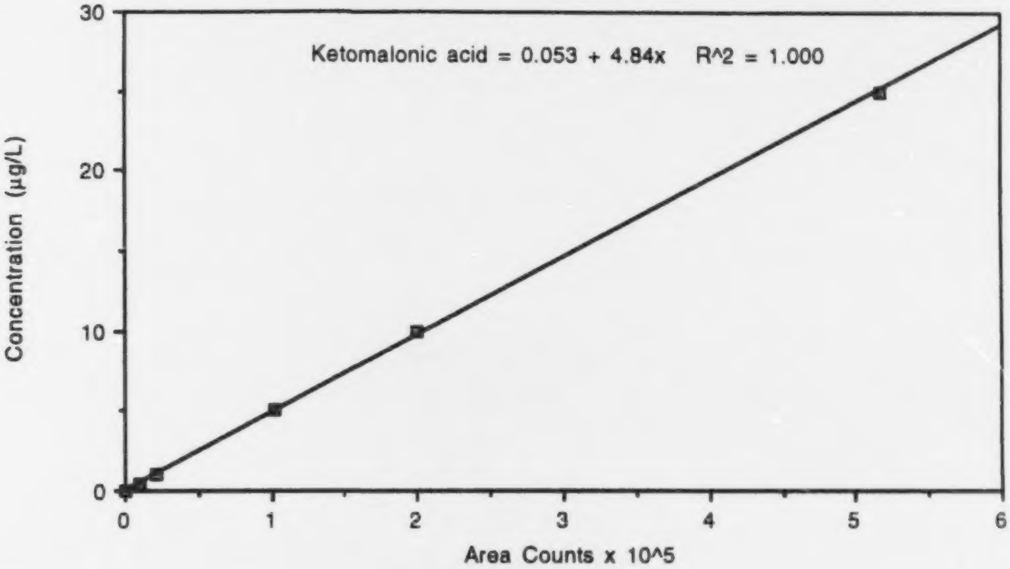


Figure I.4 Typical Calibration Curve for Ketomalonic Acid

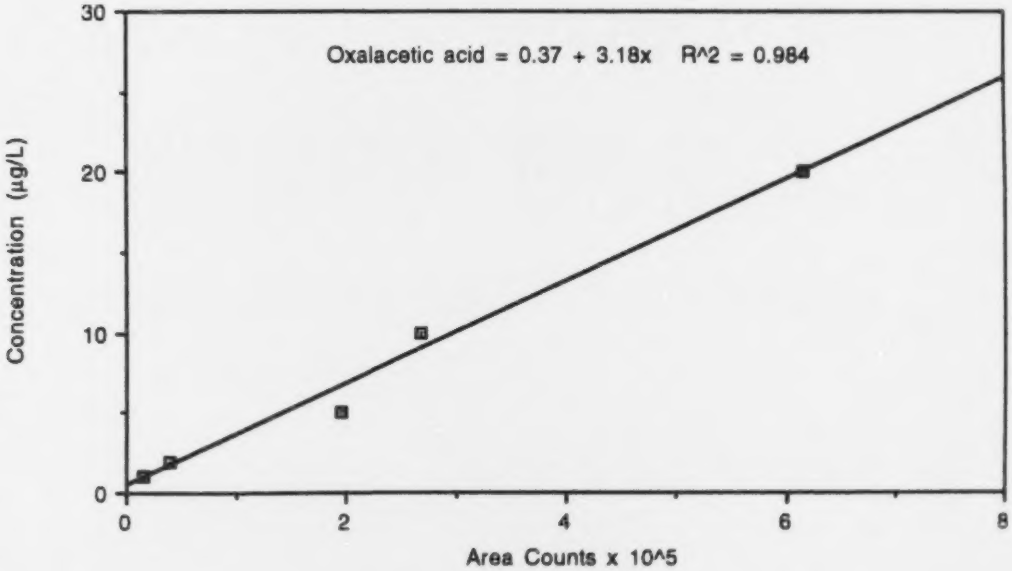
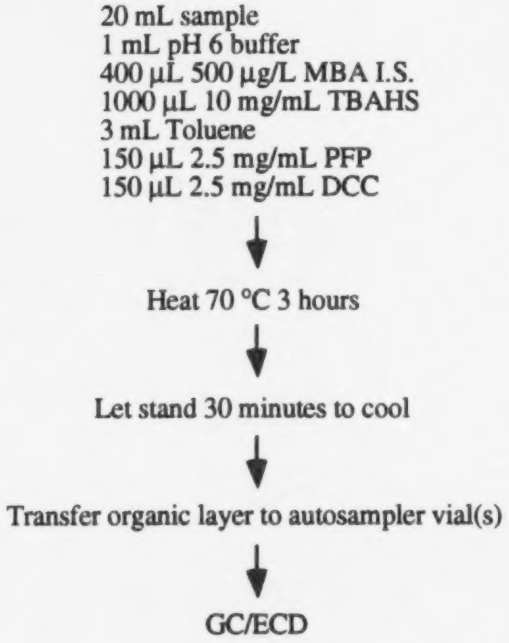


Figure I.5 Typical Calibration Curve for Oxalacetic Acid



GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 220 °C, detector 300 °C
oven: 90(5)-10-295(5)

Figure I.6 Outline of the Method for the Analysis of Carboxylic Acids

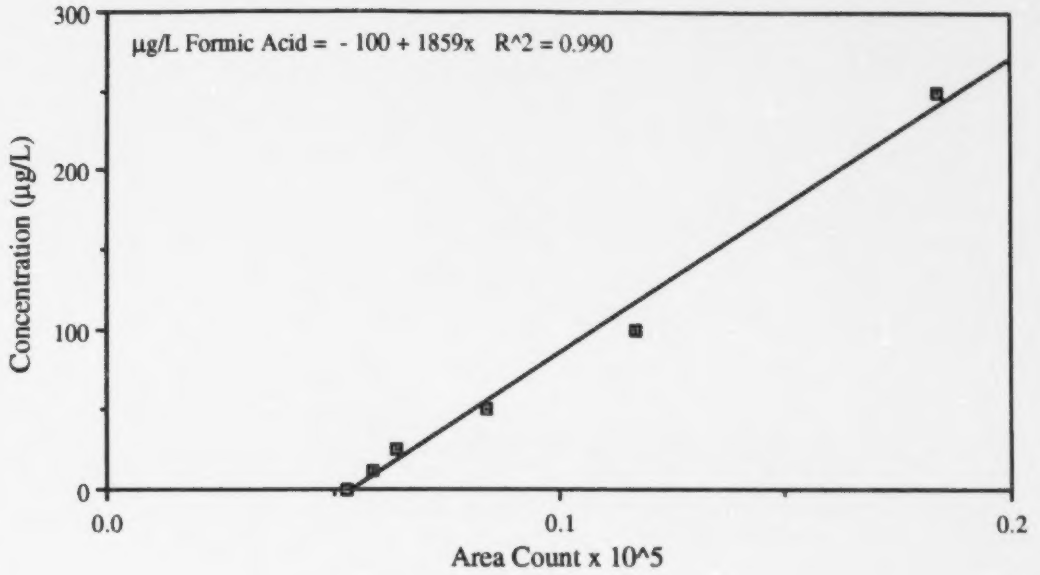


Figure I.7 Typical Calibration Curve for Formic Acid

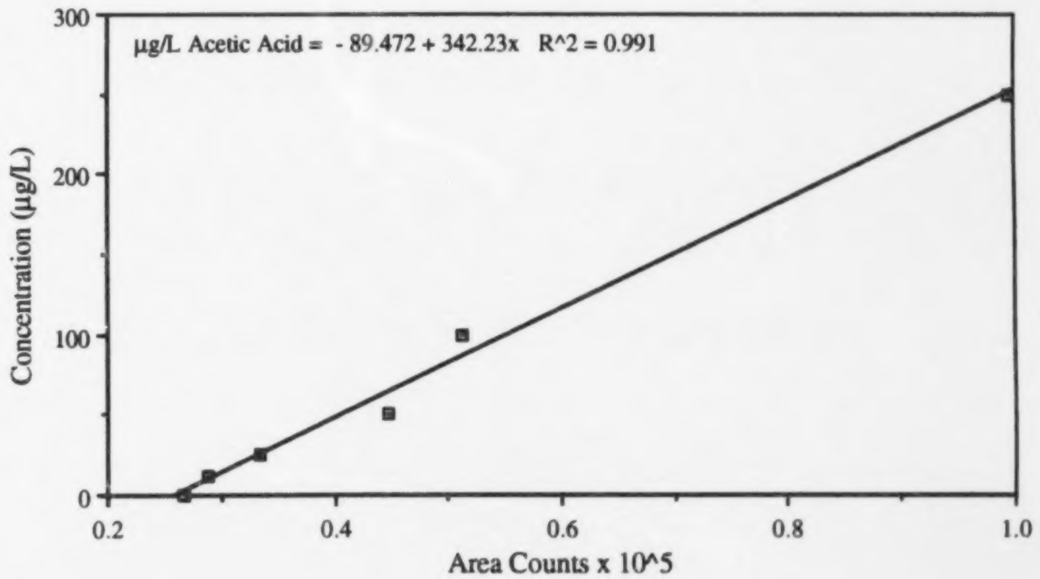


Figure I.8 Typical Calibration Curve for Acetic Acid

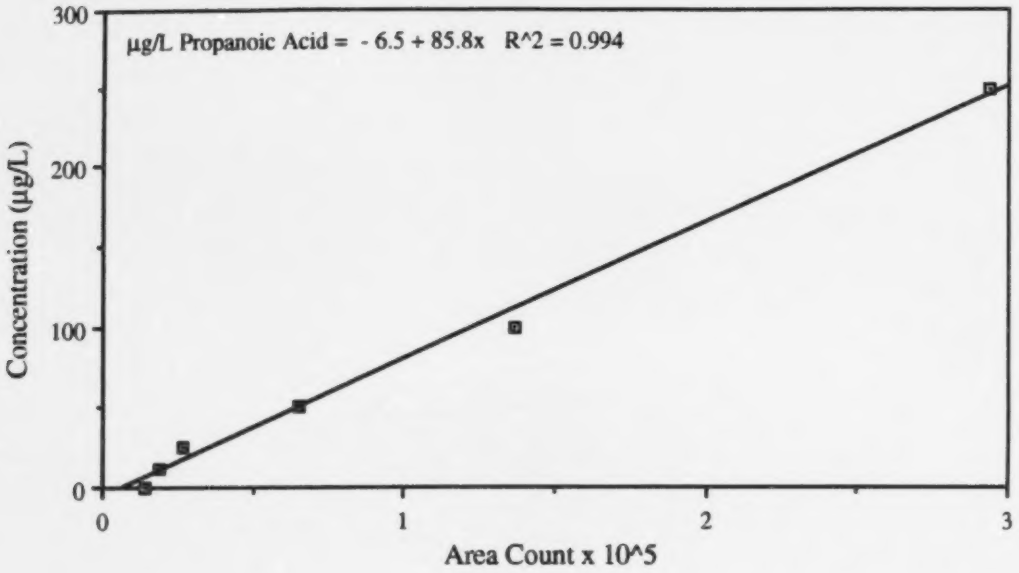


Figure I.9 Typical Calibration Curve for Propanoic Acid

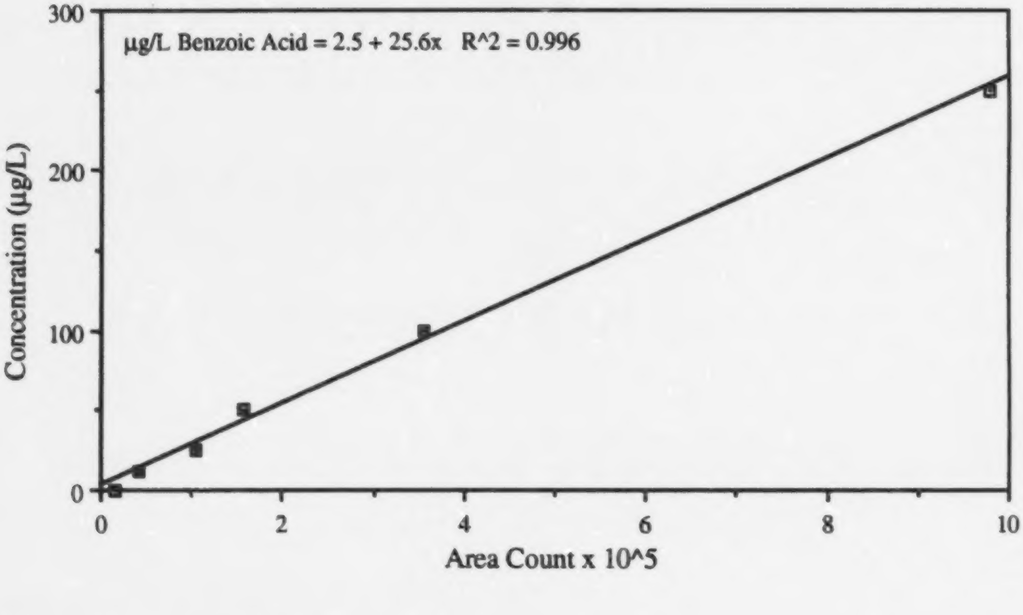


Figure I.10 Typical Calibration Curve for Benzoic Acid

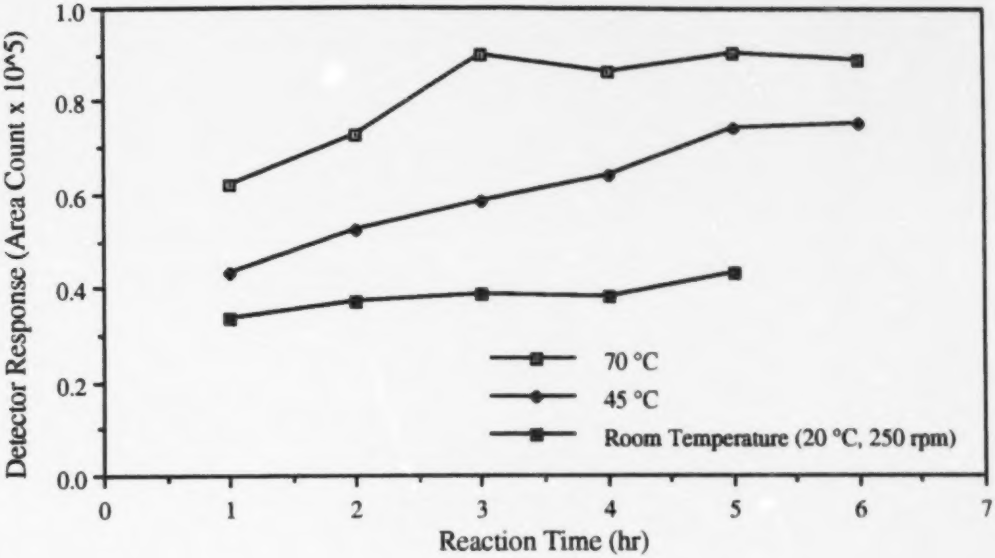


Figure I.11 Kinetics of Formation of Pentafluorophenol Ester of Acetic Acid

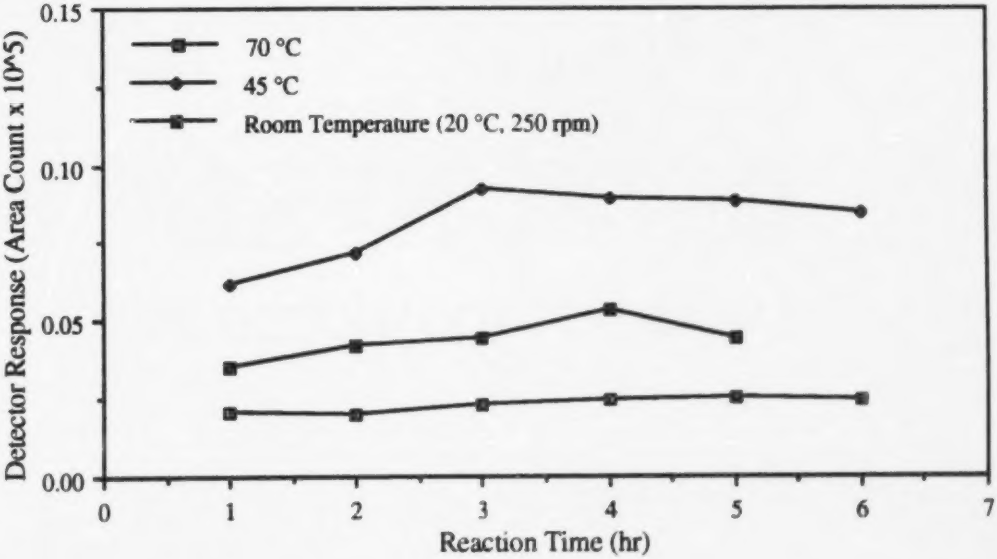


Figure I.12 Kinetics of Formation of Pentafluorophenol Ester of Formic Acid

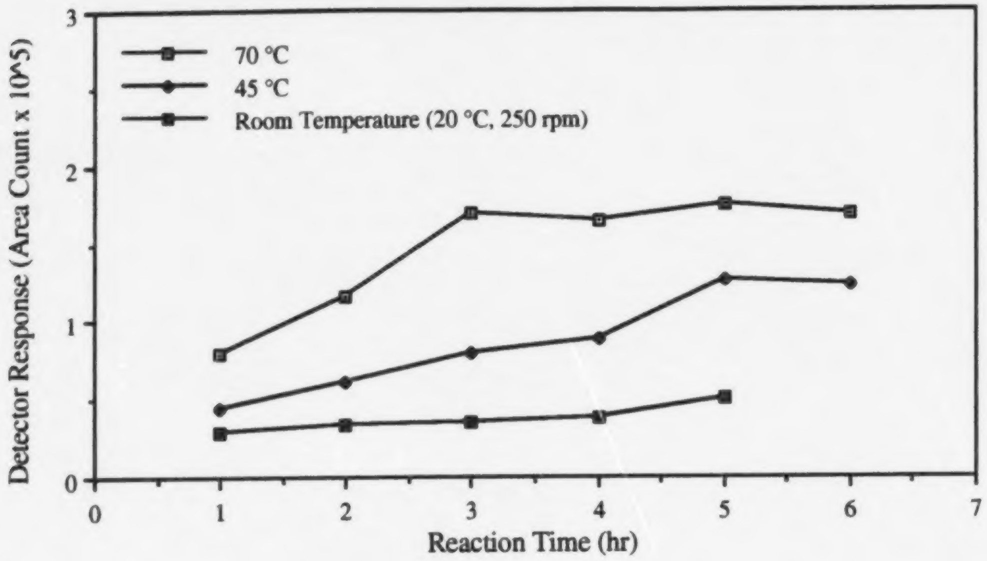


Figure I.13 Kinetics of Formation of Pentafluorophenol Ester of Propanoic Acid

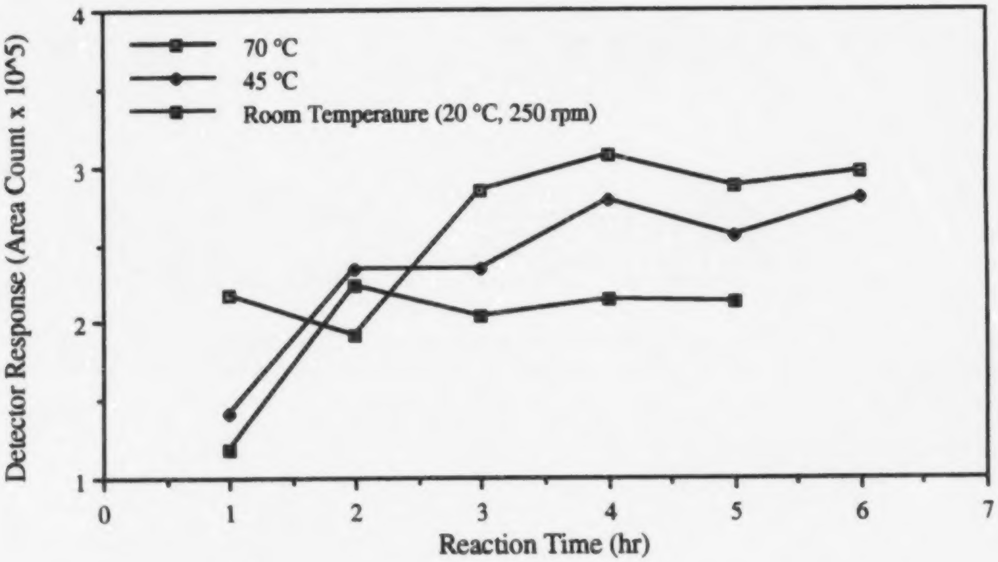


Figure I.14 Kinetics of Formation of Pentafluorophenol Ester of Benzoic Acid

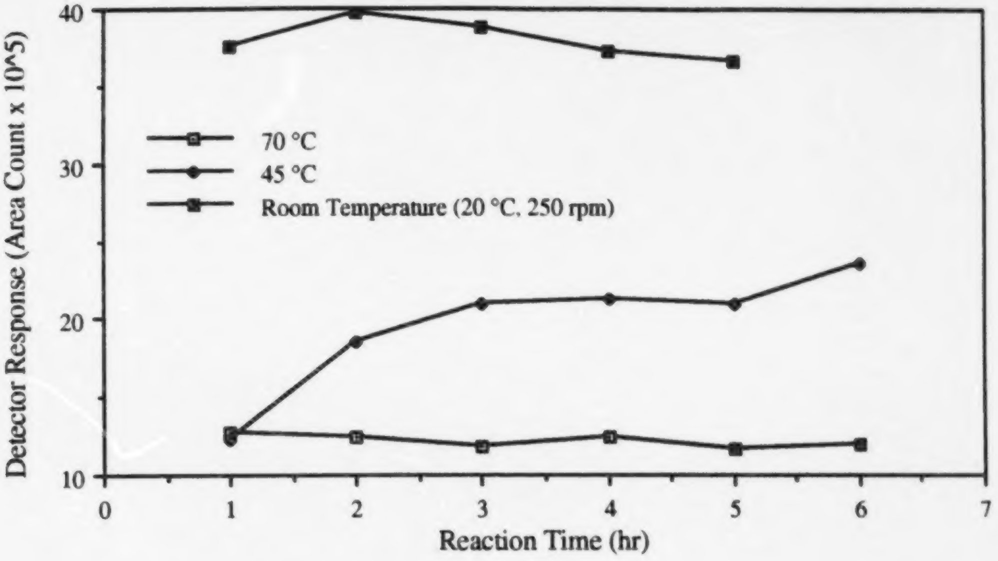


Figure I.15 Kinetics of Formation of Pentafluorophenol Ester of Mucobromic Acid

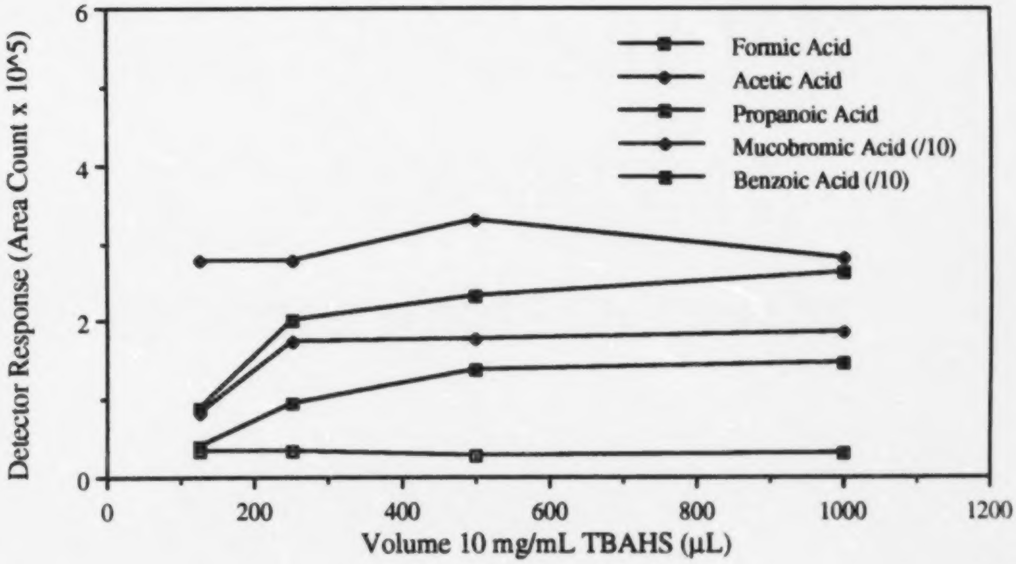


Figure I.16 Effect of TBAHS Concentration on Pentafluorophenol Esterification of Carboxylic Acids

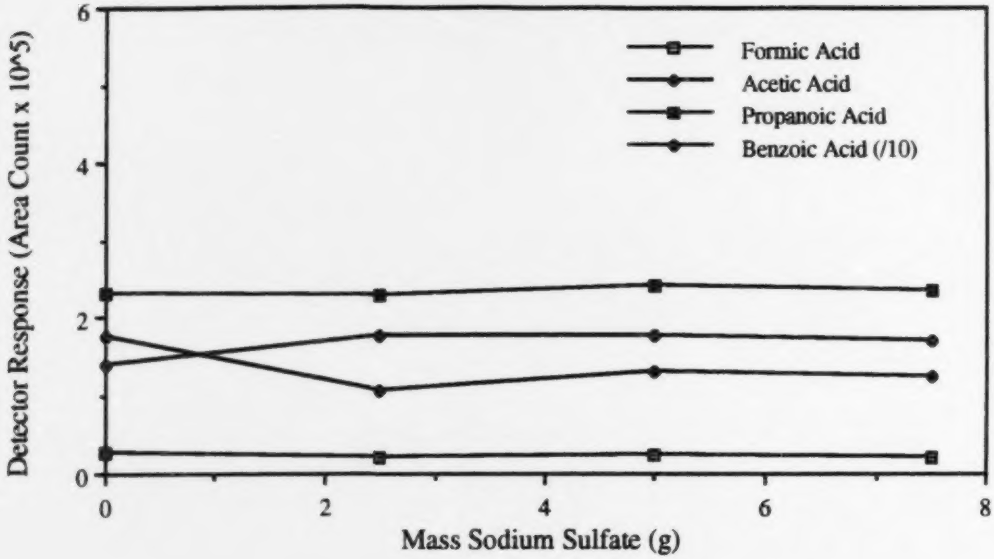


Figure I.17 Effect of Sodium Sulfate Concentration on Pentafluorophenol Esterification of Carboxylic Acids

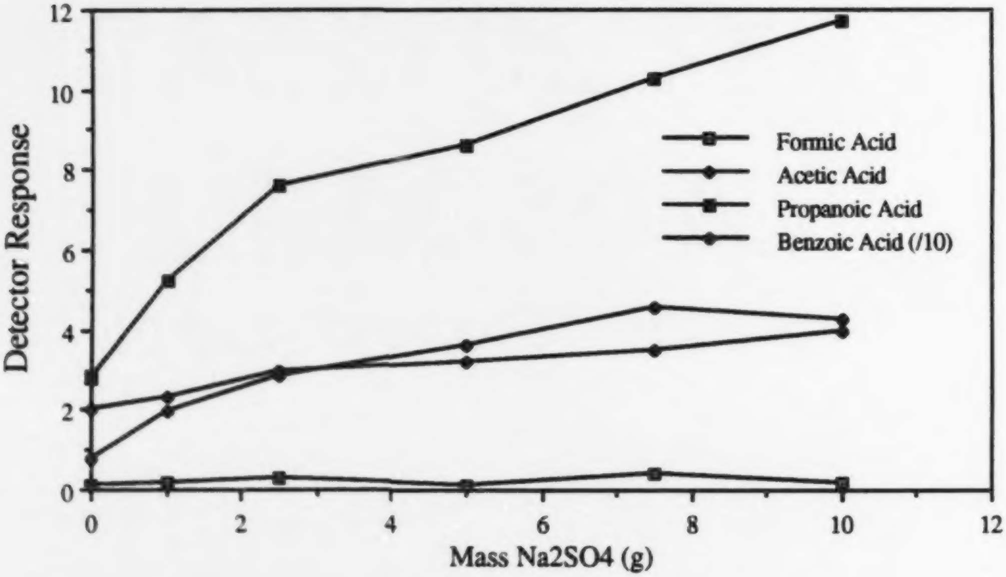
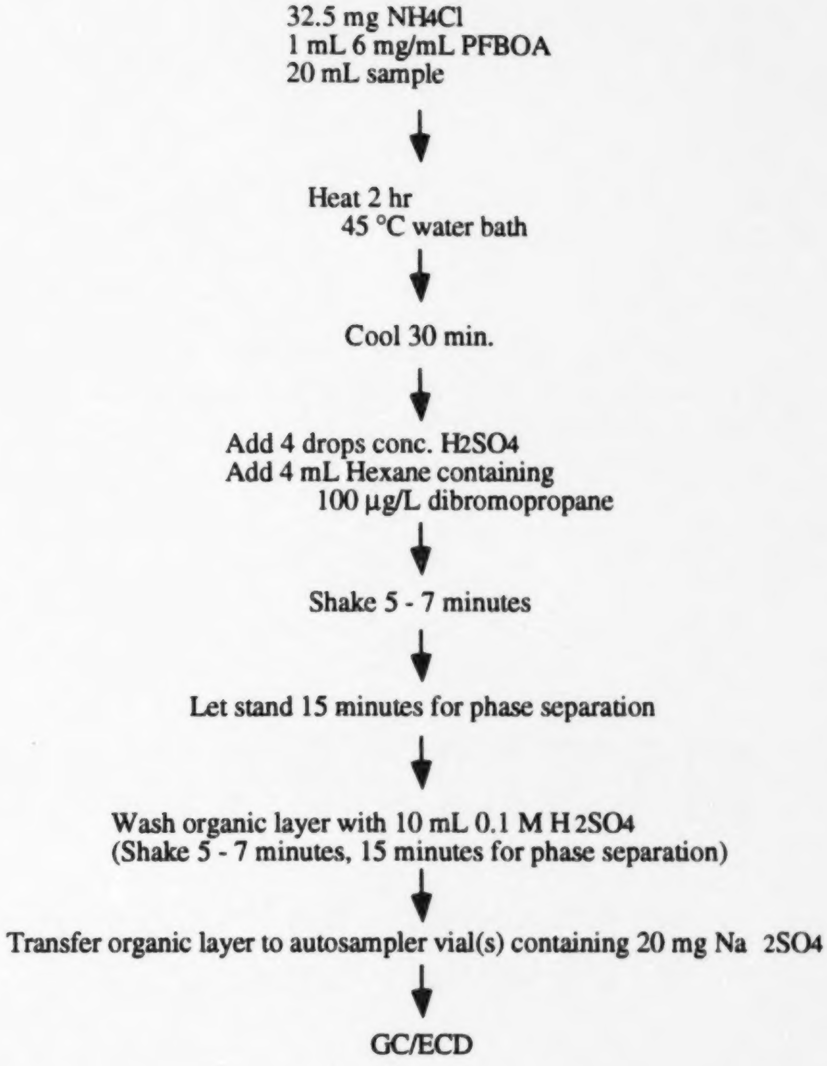


Figure I.18 Effect of Sodium Sulfate Concentration on Pentafluorophenol Esterification of Carboxylic Acids in the Absence of TBAHS


32.5 mg NH_4Cl
1 mL 6 mg/mL PFBOA
20 mL sample
Heat 2 hr
45 °C water bath
Cool 30 min.
Add 4 drops conc. H_2SO_4
Add 4 mL Hexane containing
100 µg/L dibromopropane
Shake 5 - 7 minutes
Let stand 15 minutes for phase separation
Wash organic layer with 10 mL 0.1 M H_2SO_4
(Shake 5 - 7 minutes, 15 minutes for phase separation)
Transfer organic layer to autosampler vial(s) containing 20 mg Na_2SO_4
GC/ECD

GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 250 °C, detector 300 °C
oven: 100(5)-10-295(5)

Figure I.19 Outline of the Method for the Analysis of Aldehydes

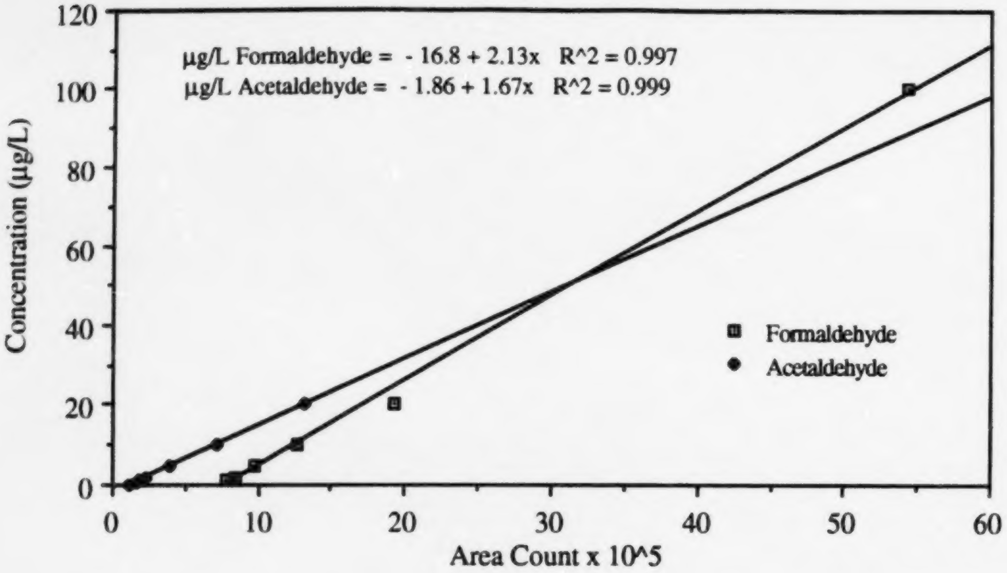


Figure I.20 Typical Calibration Curve for Formaldehyde and Acetaldehyde

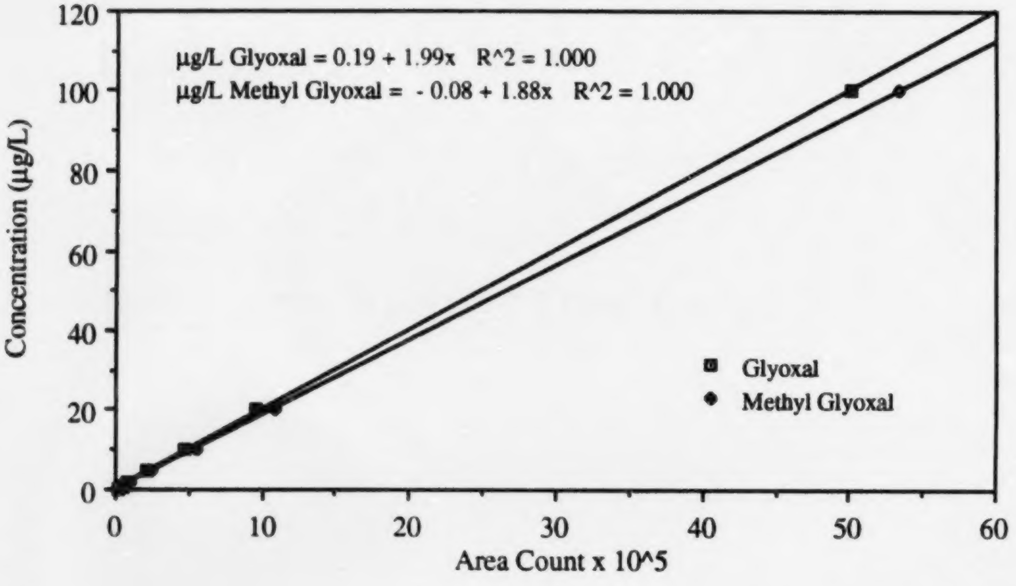


Figure I.21 Typical Calibration Curve for Glyoxal and Methyl Glyoxal

Table I.3 Recoveries of Aldehydes from Natural and Ozonated River Water

Thiosulfate preserved, no HgCl2

		Area Counts (x 10^5)			Concentrations (µg/L)			Spike Amount (µg/L)	RECOVERY (%)
Aldehyde	RT (min)	Raw (R3)	Ozonated (# 6)	O3 + Spike (# 10)	Raw	Ozonated	O3 + Spike		
Dibromopropane (IS)	4.06	1.13	1.13	1.29					
Formaldehyde	4.7	0.526	25.5	127.5	1.32	30.7	132	108	93.8
Acetaldehyde	6.14	2.48	4.99	15.6	9.06	17.4	46.4		
Acetaldehyde	6.31	2.39	5.61	21.8	8.76	19.5	64.6		
total Acetaldehyde					17.8	37.0	111	78.8	93.9
2-Methylbutanal	10.86	0	0	2.65	0.00	0.00	22.9		
2-Methylbutanal	10.95	0	0.0188	9.64	0.00	0.16	76.0		
total 2-Methylbutanal					0.00	0.16	98.9	80.0	123
Glyoxal	25.49	0.0431	1.609	38.54	0.91	2.59	54.4		
Glyoxal	25.77	0.0188	3.167	50.32	0.71	5.10	71.0		
total Glyoxal					1.62	7.69	125	114	103
Methyl glyoxal	26.56	0.0906	0.5173	36.9	0.74	3.91	88.4	105	80.8

NH4Cl preserved, no HgCl2

		Area Counts (x 10^5)			Concentrations (µg/L)			Spike Amount (µg/L)	RECOVERY (%)
Aldehyde	RT (min)	Raw (R2)	Ozonated (# 5)	O3 + Spike (# 9)	Raw	Ozonated	O3 + Spike		
Dibromopropane (IS)	4.06	1.14	1.13	1.28					
Formaldehyde	4.7	0.486	30.24	126.1	1.27	36.2	131	108	87.1
Acetaldehyde	6.14	0	1.62	20.3	0.00	6.19	60.2		
Acetaldehyde	6.31	0	1.46	16.6	0.00	5.66	49.3		
total Acetaldehyde					0.00	11.8	110	78.8	124
2-Methylbutanal	10.86	0	0.0296	0.415	0.00	3.06	5.95		
2-Methylbutanal	10.95	0	0.00596	9.95	0.00	2.85	78.4		
total 2-Methylbutanal					0.00	5.91	84.3	80.0	98.0
Glyoxal	25.49	0.0259	1.381	35.46	0.77	2.22	50.0		
Glyoxal	25.77	0.0125	1.674	44.66	0.66	2.70	63.0		
total Glyoxal					1.43	4.92	113	114	94.8
Methyl glyoxal	26.56	0.078	0.573	25.63	0.66	4.06	62.2	105	55.6

32.5 mg NH_4Cl
400 µL 500 µg/L BrAA I.S.
20 mL sample
6 g Na_2SO_4
1.5 mL conc H_2SO_4
5 mL MTBE containing
100 µg/L dibromopropane I.S.

↓

Shake 5 - 7 minutes

↓

Let stand 15 minutes for phase separation

↓

Dry 1.5 mL ether layer by passing it
through a Pasteur pipet half-filled with Na_2SO_4
into autosampler vial

↓

Cool extracts in freezer 3 minutes

↓

Add 100 µL CH_2N_2

↓

React 4°C, 30 minutes

↓

Add 0.01 g silica gel

↓

GC/ECD

GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 157 °C, detector 300 °C
oven: 50(10)-5-295(5)

Figure I.22 Outline of the Method for the Analysis of Haloacetic Acids

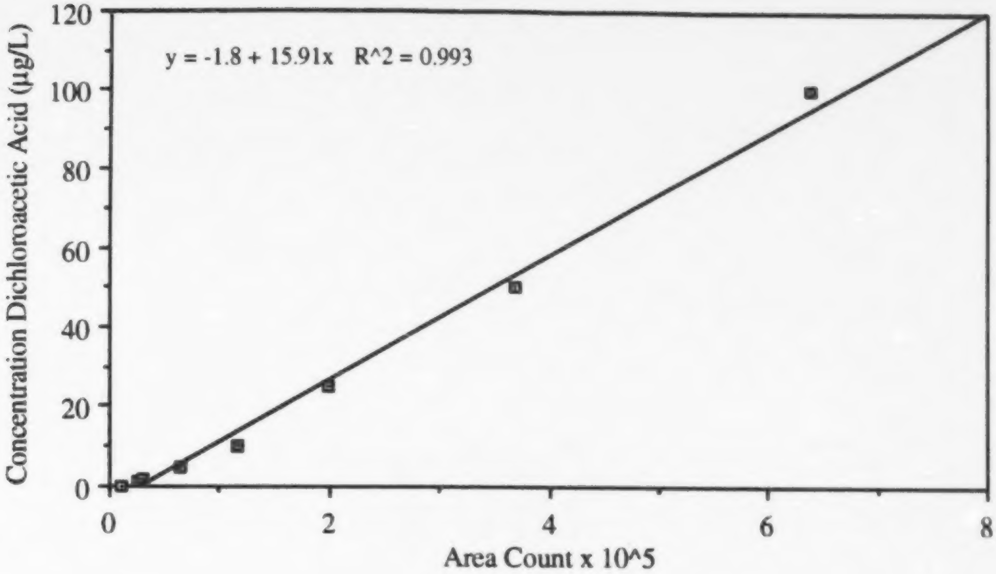


Figure I.23 Typical Calibration Curve for Dichloroacetic Acid

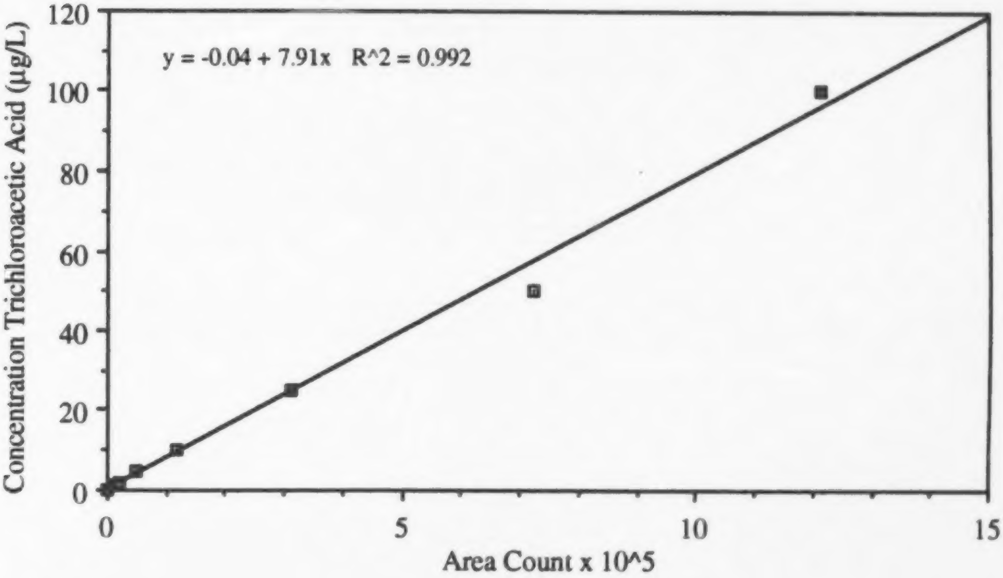


Figure I.24 Typical Calibration Curve for Trichloroacetic Acid

32.5 mg NH_4Cl
20 mL sample
5 g Na_2SO_4
4 mL pentane containing
100 µg/L dibromopropane I.S.

↓

Shake 5 - 7 minutes

↓

Let stand 15 minutes for phase separation

↓

Transfer to autosampler vial(s) containing 20 mg Na_2SO_4

↓

GC/ECD

GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 220 °C, detector 300 °C
oven: 50(5)-5-295(5)

Figure I.25 Outline of the Method for the Analysis of Trihalomethanes

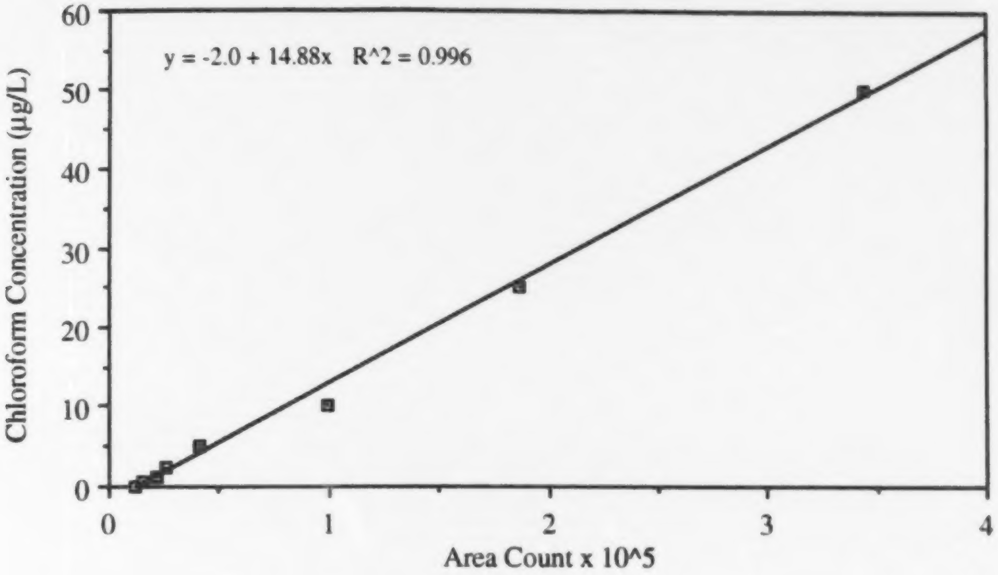


Figure I.26 Typical Calibration Curve for Chloroform

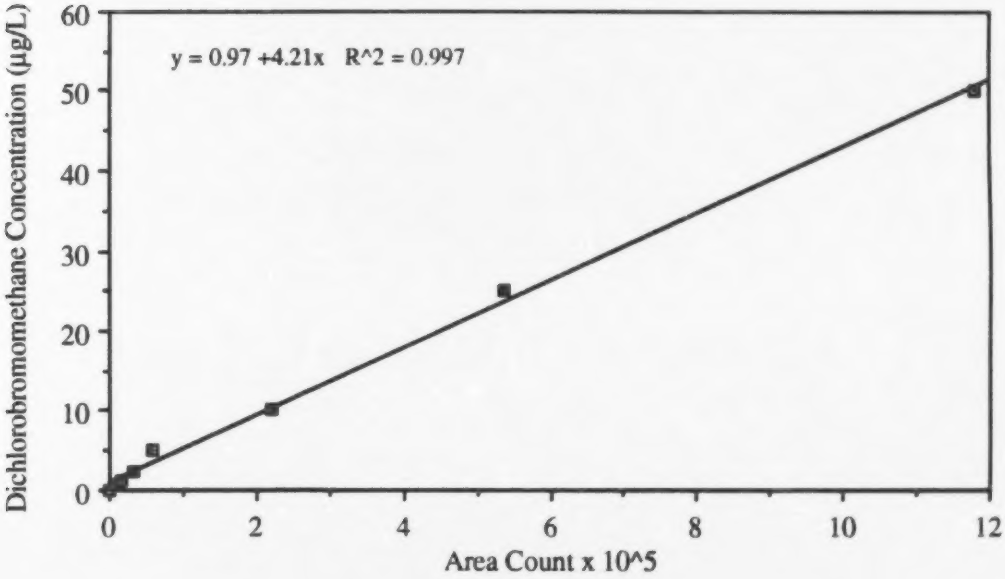


Figure I.27 Typical Calibration Curve for Dichlorobromomethane

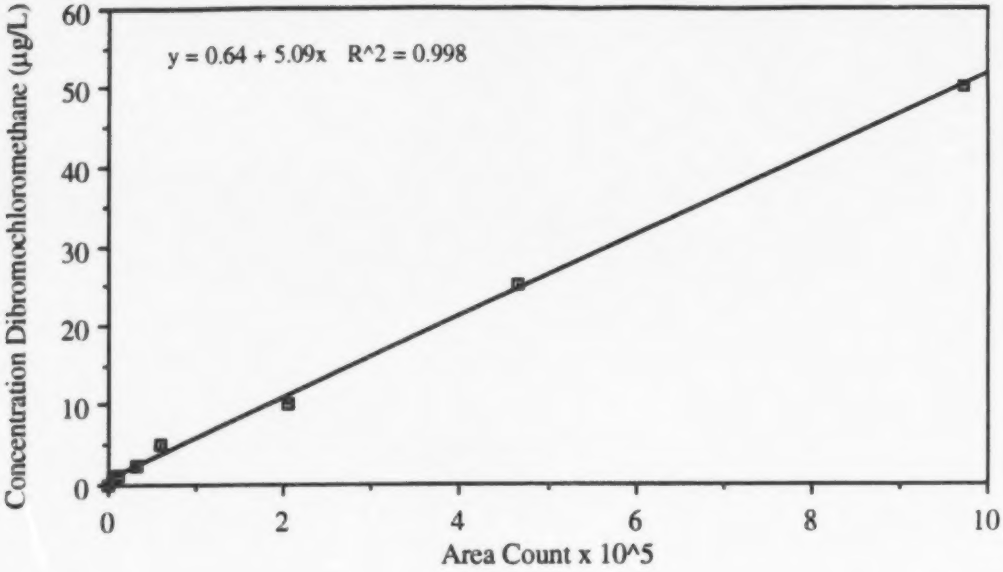


Figure I.28 Typical Calibration Curve for Dibromochloromethane

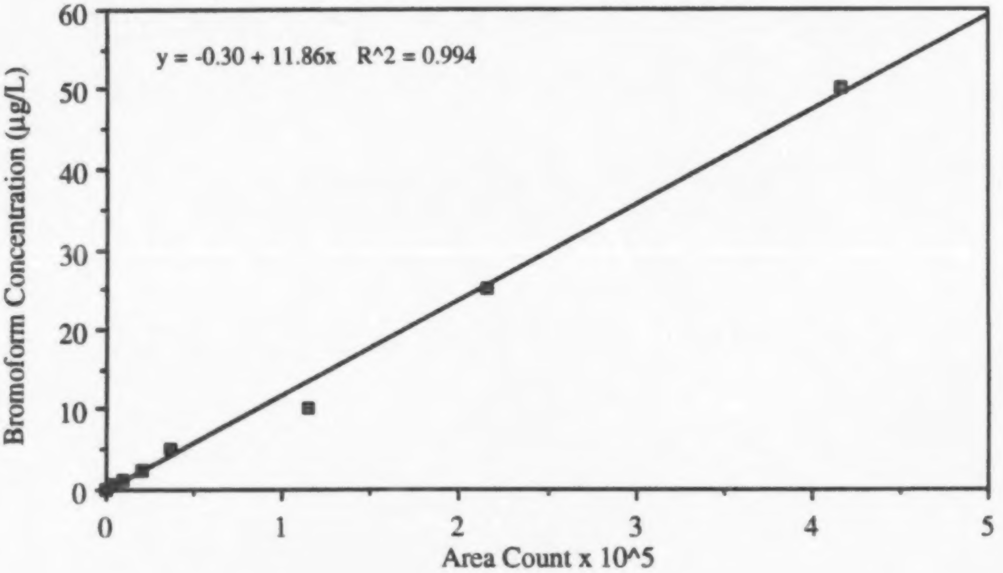


Figure I.29 Typical Calibration Curve for Bromoform

10 mg ascorbic acid
20 mL sample
5 g Na_2SO_4
4 mL MTBE containing
100 µg/L dibromopropane I.S.

↓

Shake 5 - 7 minutes

↓

Let stand 15 minutes for phase separation

↓

Transfer to autosampler vial(s) containing 20 mg Na_2SO_4

↓

GC/ECD

GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 220 °C, detector 300 °C
oven: 50(5)-5-295(5)

Figure I.30 Outline of the Method for the Analysis of Chloral Hydrate

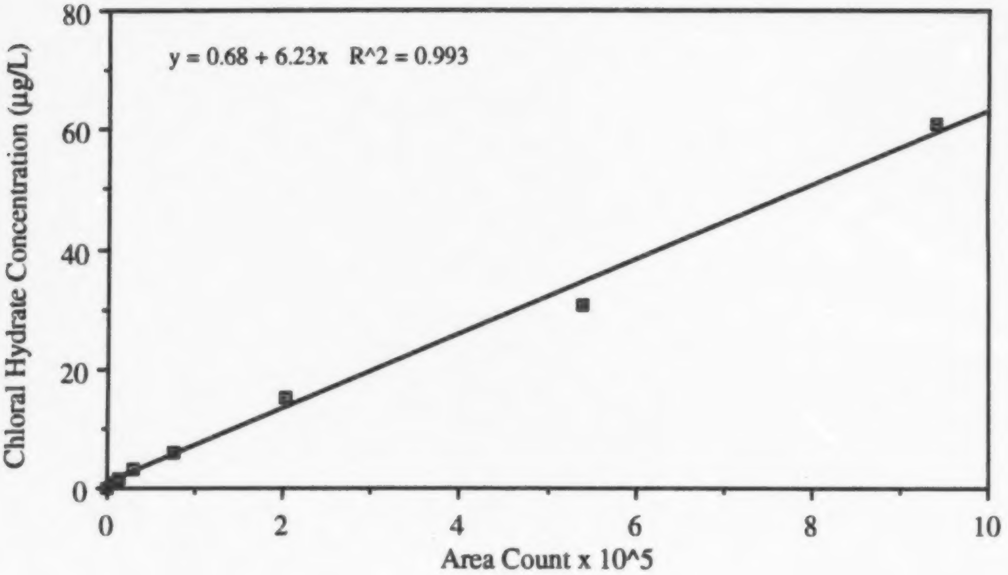


Figure I.31 Typical Calibration Curve for Chloral Hydrate

10 mg ascorbic acid
20 mL sample
5 g Na_2SO_4
4 mL cyclohexane

↓

Shake 5 - 7 minutes

↓

Let stand 15 minutes for phase separation

↓

Transfer to autosampler vial(s) containing 20 mg Na_2SO_4

↓

GC/ECD

GC/ECD:

30m x 0.25mm x 1μm DB-5 capillary column
2 μL injection, split 1:1
injector 157 °C, detector 300 °C
oven: 35 °C isothermal

Figure I.32 Outline of the Method for the Analysis of Cyanogen Chloride

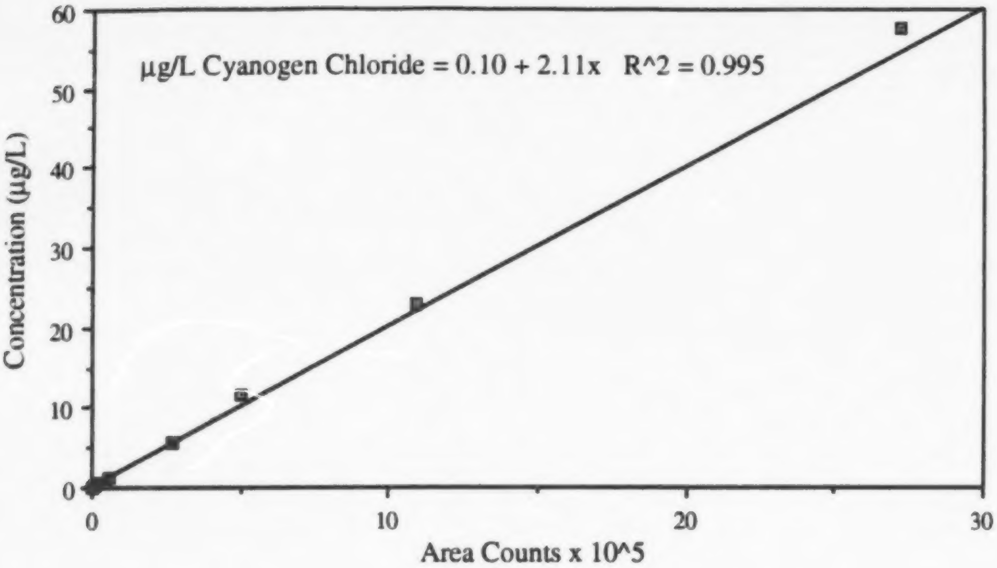


Figure I.33 Typical Calibration Curve for Cyanogen Chloride

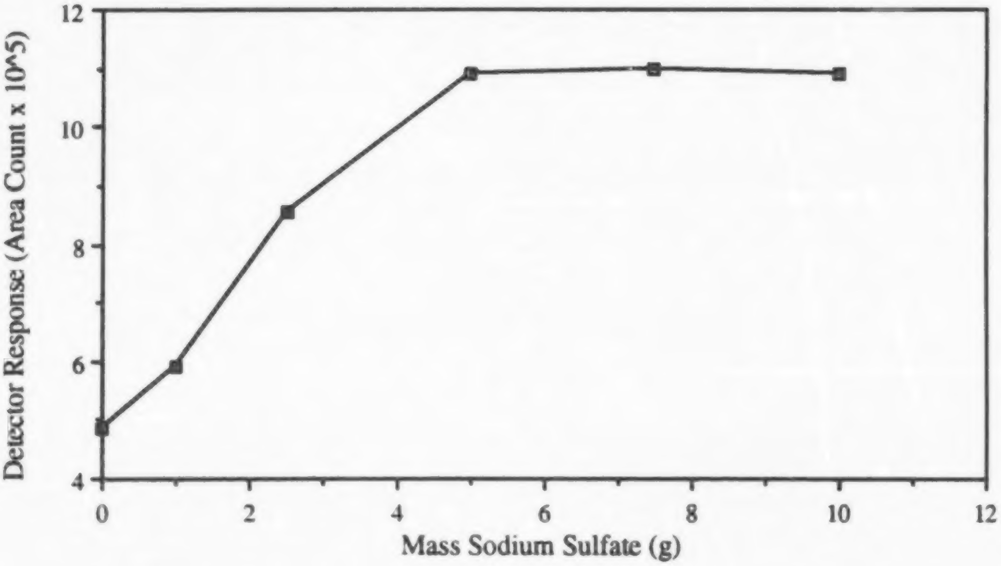
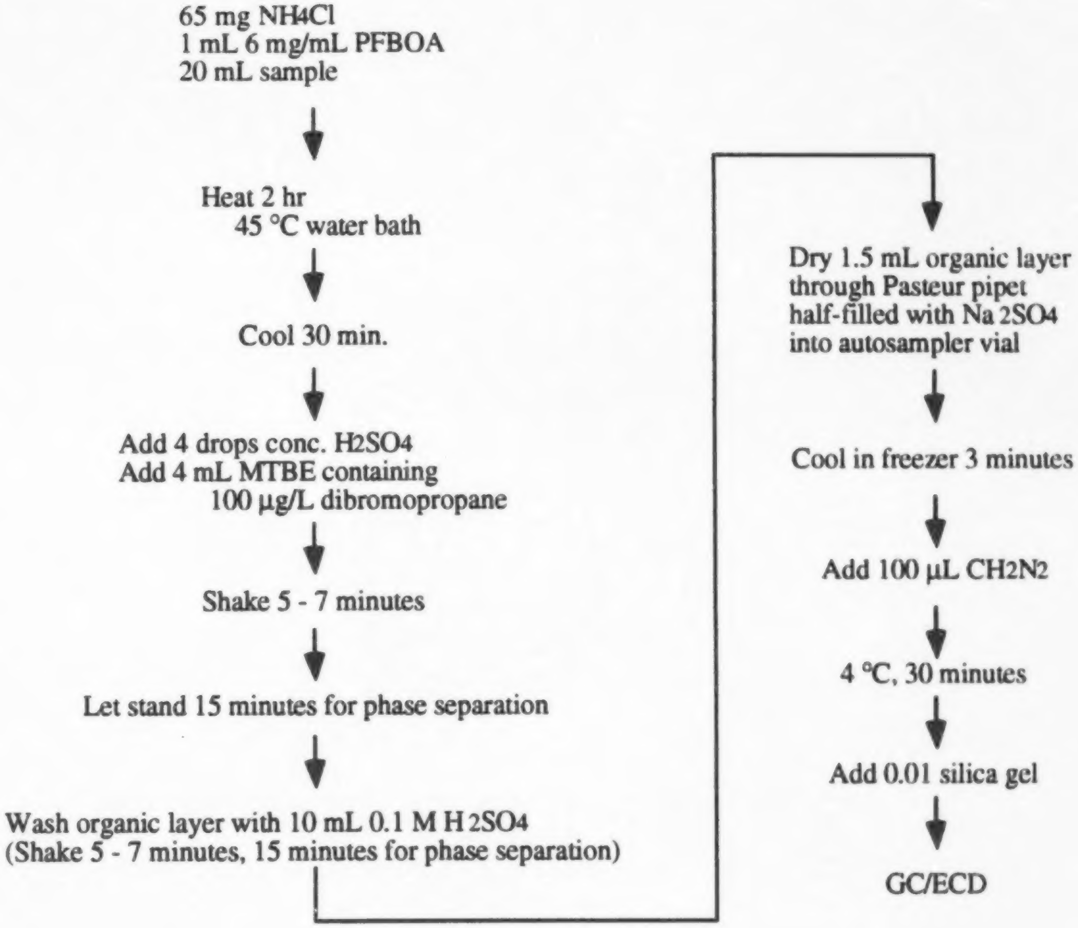


Figure I.34 Effect of Ionic Strength on Cyanogen Chloride Extraction Efficiency



GC/ECD:

30m x 0.25mm x 1µm DB-5 capillary column
2 µL injection, split 1:1
injector 250 °C, detector 300 °C
oven: 100(5)-10-295(5)

Figure I.35 Outline of the Method for the Analysis of Chloro-oxoacids

APPENDIX II

NOM ADSORPTION MONITORING DATA

Table II.1 Characterization of Water From Driedmeat Lake
September 26, 1991*

Parameter	Value
Alkalinity	260 mg/L
Calcium	84 mg/L
Colour	55 TCU
Conductivity	316 µS/cm
Fluoride	0.17 mg/L
Total Hardness	156 mg/L
Magnesium	72 mg/L
pH	8.54
Temperature	13.6 °C
Turbidity	7.4 NTU
Phosphorus (Sept.24)	116.6 µg/L
Total Solids (Sept.24)	272 mg/L
Total Dissolved Solids (Sept.24)	261 mg/L
Total Suspended Solids (Sept.24)	4 mg/L

*Source: City of Camrose, Utility Summary Monthly Report, September, 1991

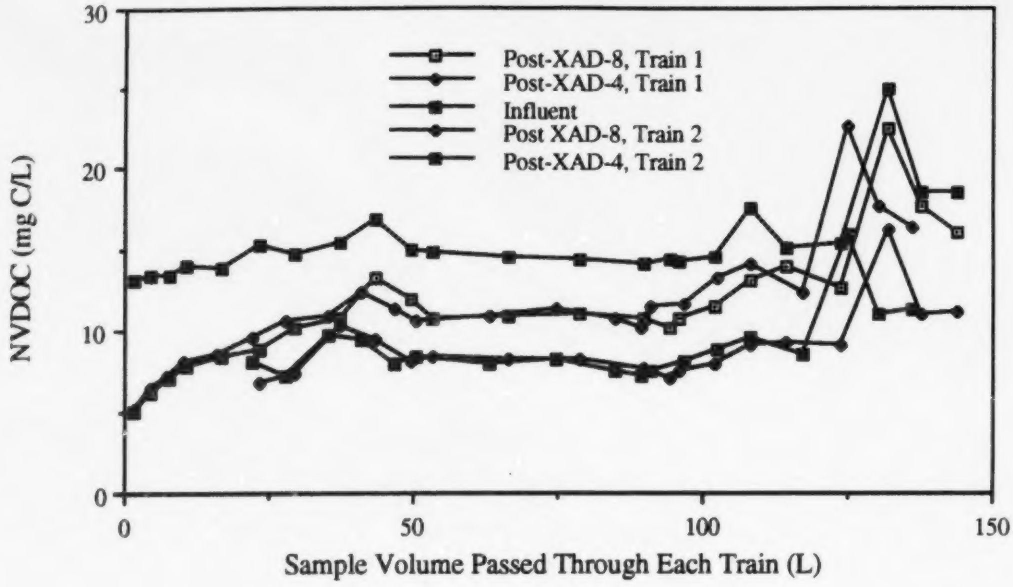


Figure II.1 NVDOC Monitoring Data for the Adsorption of Driedmeat Lakewater NOM

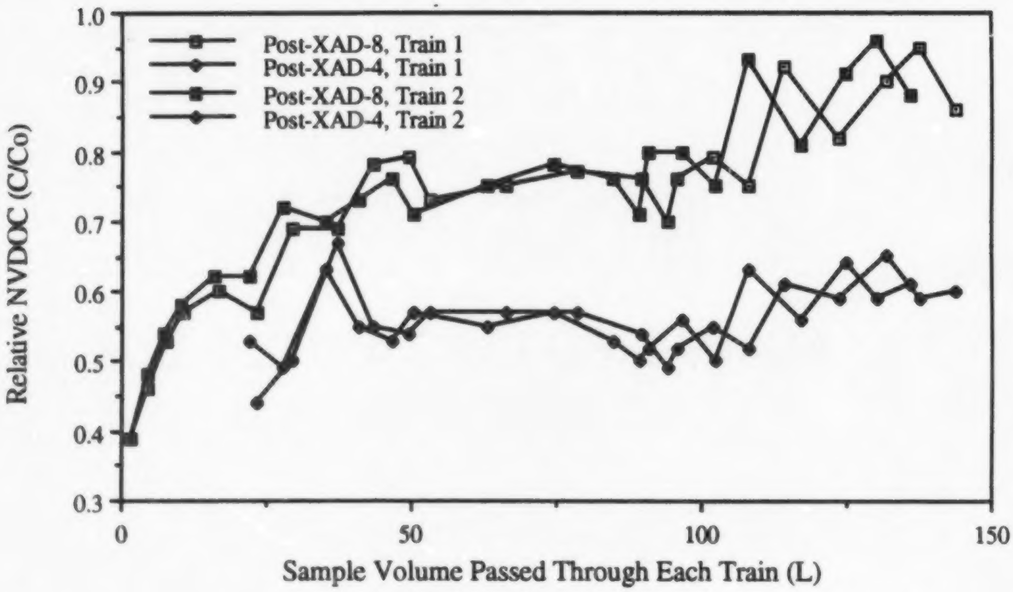


Figure II.2 NVDOC Monitoring Data for the Adsorption of Driedmeat Lakewater NOM (Plotted Relative to Influent)

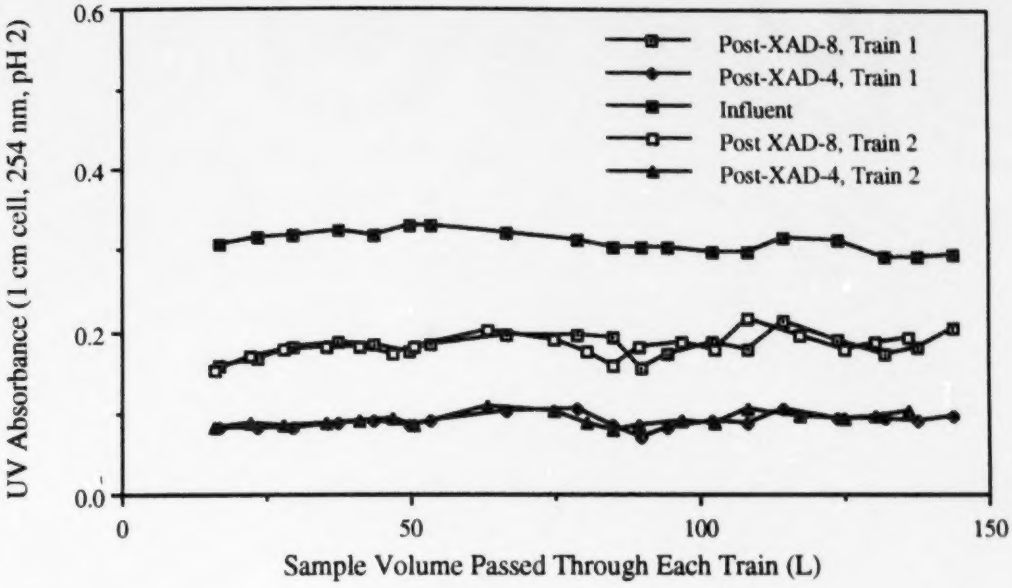


Figure II.3 UV Absorbance Monitoring Data for the Adsorption of Driedmeat Lakewater NOM (254 nm, pH 2)

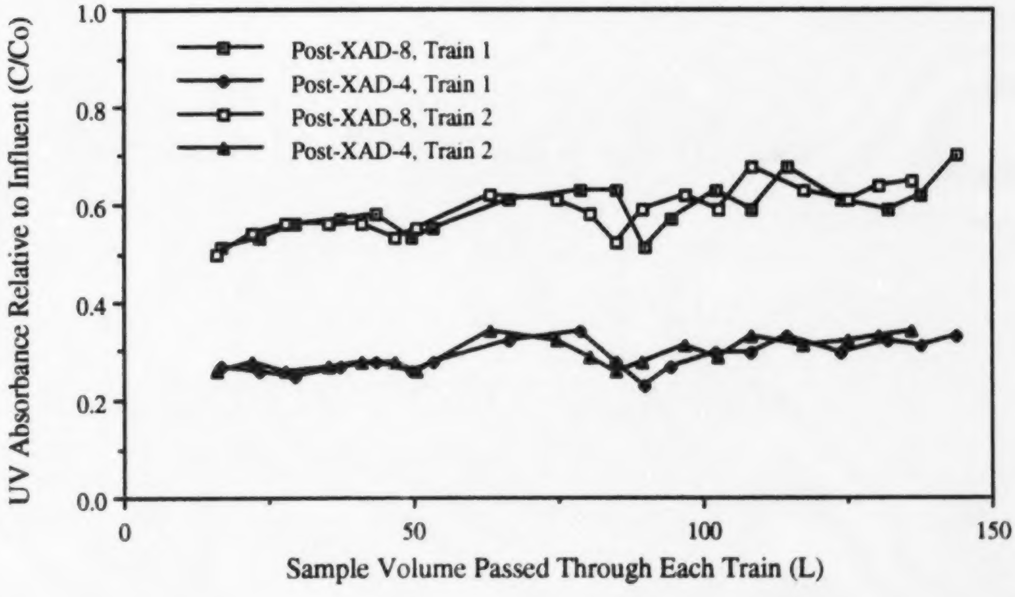


Figure II.4 UV Absorbance Monitoring Data for the Adsorption of Driedmeat Lakewater NOM (Plotted Relative to Influent, 254 nm, pH 2)

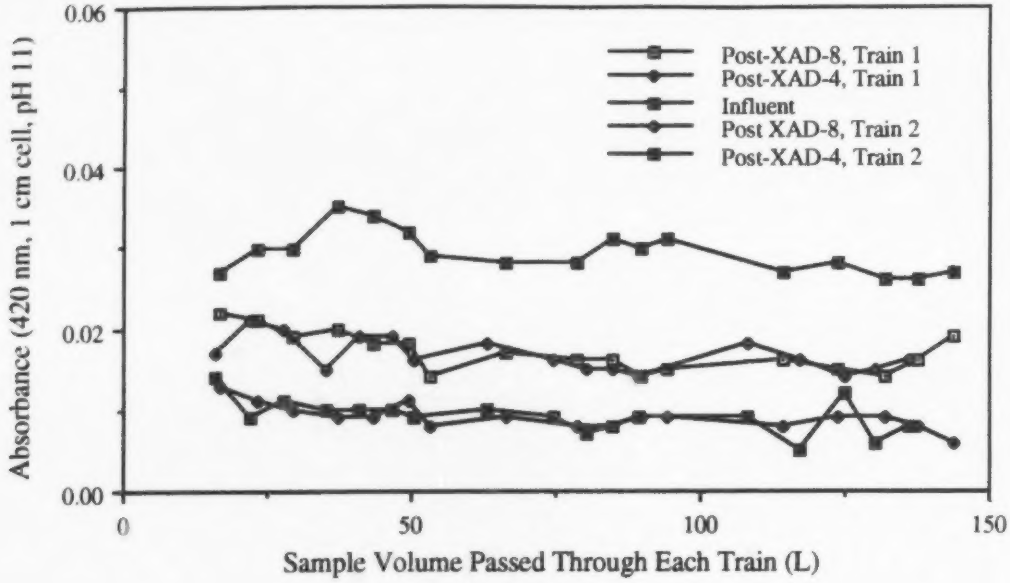


Figure II.5 Colour Monitoring Data for the Adsorption of Driedmeat Lakewater NOM (420 nm, pH 11)

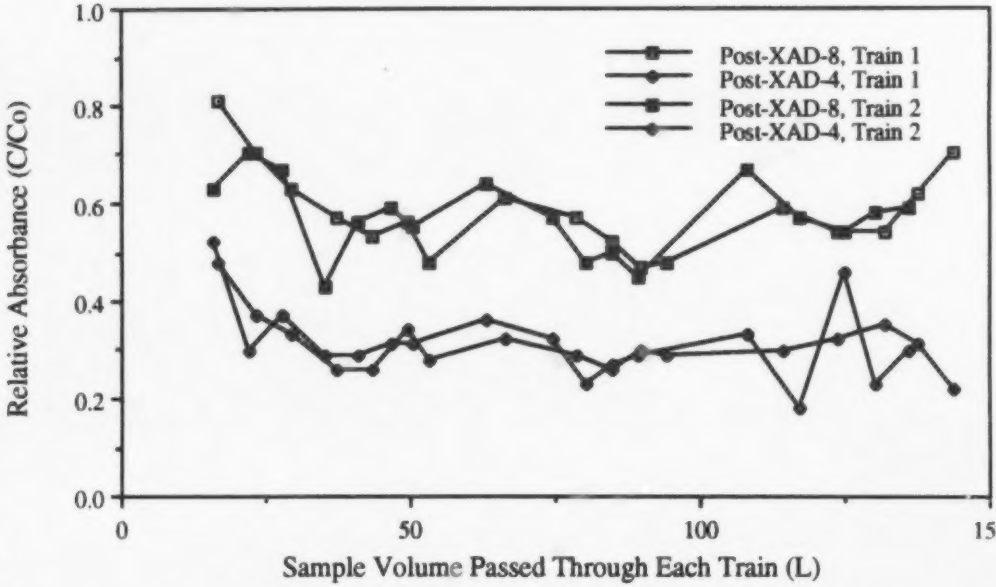


Figure II.6 Colour Monitoring Data for the Adsorption of Driedmeat Lakewater NOM (Plotted Relative to Influent, 420 nm, pH 11)

Table II.2 Desorption Data for Driedmeat Lakewater Fulvic Acids

Fraction	Volume Collected (mL)	NVDOC† (mg/L)		Theor. Mass Isolated (as mg C)	UV Absorbance (254 nm)	Colour (pH 11; 420 nm)
		1	2			
XAD-8 Desorption						
A	370	116.6	117.1	43.2	2.74††	0.247
B - TRAIN 1	300	320.4*	620.1**	378.3	3.97	3.62††
B - TRAIN 2	235	718.2**	724.9**	339.1	4.11	4.02
C - 1	915	163.1	161.2	148.4	3.18	0.345
C - 2	790	63.6	65.2	50.9	1.34	0.104
C - 3	1000	38.1	38.6	38.3	0.71	0.056
D	950	17.1	17.2	16.3	0.34	0.013
Totals	4560			1014.5		
		center cut % of total		70.7		
XAD-4 Desorption						
A	185	40.9	41.9	7.7	0.583	0.137
B - TRAIN 1	395	669.0	673.6	265.2	3.28	0.753
B - TRAIN 2	280	966.9	932.0	265.8	3.46	1.11
C	825	229.7	230.8	190.0	3.14	0.198
D	670	68.3	67.7	45.5	1.1	0.05
Totals	2355			774.2		
		center cut % of total		68.6		
XAD-8 Reconcentration						
A	200	28.8	NM	5.8	NM	NM
B	365	620.4	620.3	226.4	3.53	1.52
C	415	36.9	NM	15.3	NM	NM
Totals	980			247.5		
		center cut % of total		91.5		
XAD-4 Reconcentration						
A	310	55.5	NM	17.2	NM	NM
B	200	878.1	454.0**	178.6	3.33	0.798
C	370	75.5	NM	27.9	NM	NM
Totals	880			223.8		
		center cut % of total		79.8		

† Values for each duplicate measurement are shown (1,2)

†† High UV absorbance and Colour values may not be within the spectrophotometer linear range

* Injection volume 50 μL instead of nominal 200 μL

** Injection volume 100 μL instead of nominal 200 μL

NM = Not Measured

Table II.3 Characterization of Raw Water From the North Saskatchewan River
December 13, 1991 to February 21, 1992

Date	No.19L Carbs	No. 24L Carbs	Liters Collected	Temp (°C)*	pH*	NVDOC (mgC/L)**	UV 254 (pH2)**	Colour 420 (pH 11)***	Cond. (μmho)*
13-Dec-91	8	2	200	2.7	8.08	1.72	0.056	0.023	360
7-Jan-92	8	2	200	2.0	8.08	1.21	0.029	0.045	250
15-Jan-92	8	1	176	2.0	8.05	1.53	0.041	0.048	240
20-Jan-92	8	1	176	2.0	8.01	1.51	0.038	0.050	250
23-Jan-92	9	1	195	2.5	7.75	1.38	0.041	0.061	275
27-Jan-92	9	1	195	2.0	7.78	1.26	0.036	0.045	220
30-Jan-92	9	1	195	2.7	7.75	1.24	0.032	0.044	280
5-Feb-92	9	1	195	5.0	7.97	1.17	0.031	0.061	225
10-Feb-92	9	1	195	0.7	7.78	1.20	0.029	0.041	255
13-Feb-92	**10**	1	242	1.0	8.03	1.29	0.035	0.049	230
17-Feb-92	*10*	1	228	1.7	8.12	1.34	0.037	0.046	270
21-Feb-92	*10*	1	216	1.6	8.12	1.17	0.035	0.045	280

* Determined on single sample.
** Mean of Influent values for the period (3 to 4 samples per batch).
*** Single sample, 5 cm cell.
Bold = includes 2 x 14L carbuoys
Italics = includes 1 x 14L carbuoys

Table II.4 Characterization of Water From the North Saskatchewan River December 13, 1991 to February 21, 1992*

Parameter	1991 Dec. 13	1992 Jan. 7	Jan. 15	Jan. 20	Jan. 23	Jan. 27	Jan. 30	Feb. 5	Feb. 10	Feb. 13	Feb. 17	Feb. 21
Alkalinity, mg/L	134	128	140	144	134	130	128	124	122	124	130	130
Calcium, mg/L	112	114	128	130	119	112	116	116	114	116	120	110
Colour, TCU	2.0	2.5	3.0	2.5	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Conductivity, µS/cm	321	328	343	340	352	334	325	319	323	331	341	332
Total Hardness, mg/L	166	164	180	180	172	162	158	160	162	162	170	162
pH	8.10	8.1	8.15	8.1	8.0	8.0	8.0	8.0	8.0	8.0	8.05	8.0
Temperature, °C	0.7	0.8	0.6	0.8	0.7	0.3	0.8	0.8	0.9	0.4	0.8	0.8
Turbidity, NTU	7.0	2.6	2.1	2.6	2.7	2.7	1.9	3.3	4.9	1.9	2.5	2.5

*Source: City of Edmonton, Utility Summary Monthly Reports, December, 1991 to February, 1992.
**Monthly Mean and Range

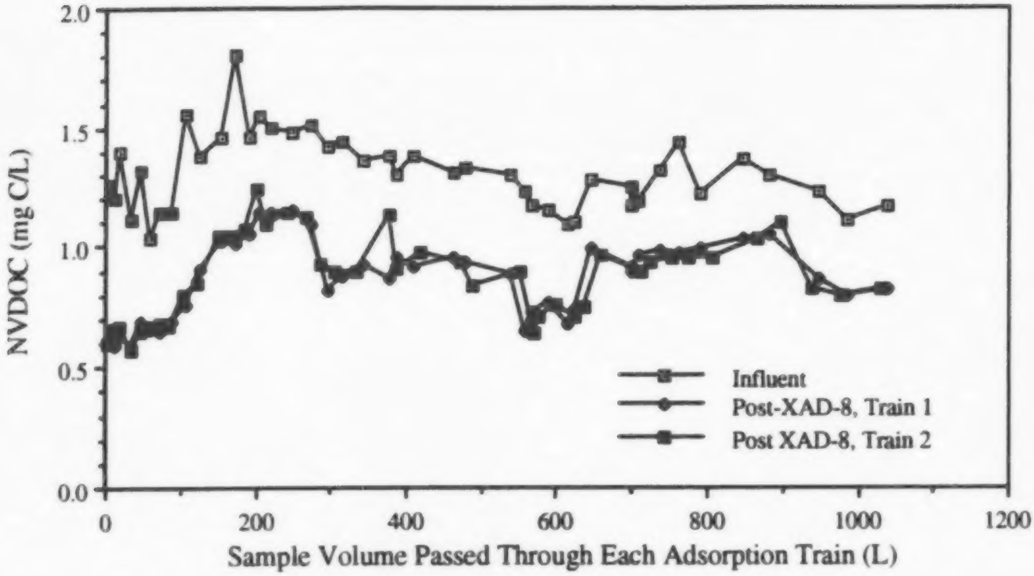


Figure II.7 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-8 Resin

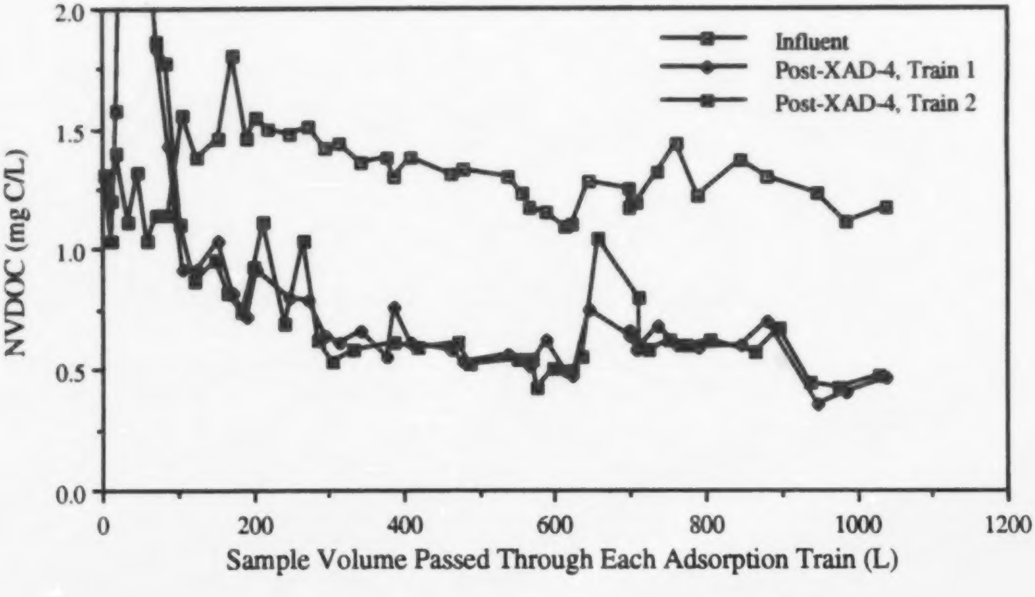


Figure II.8 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-4 Resin

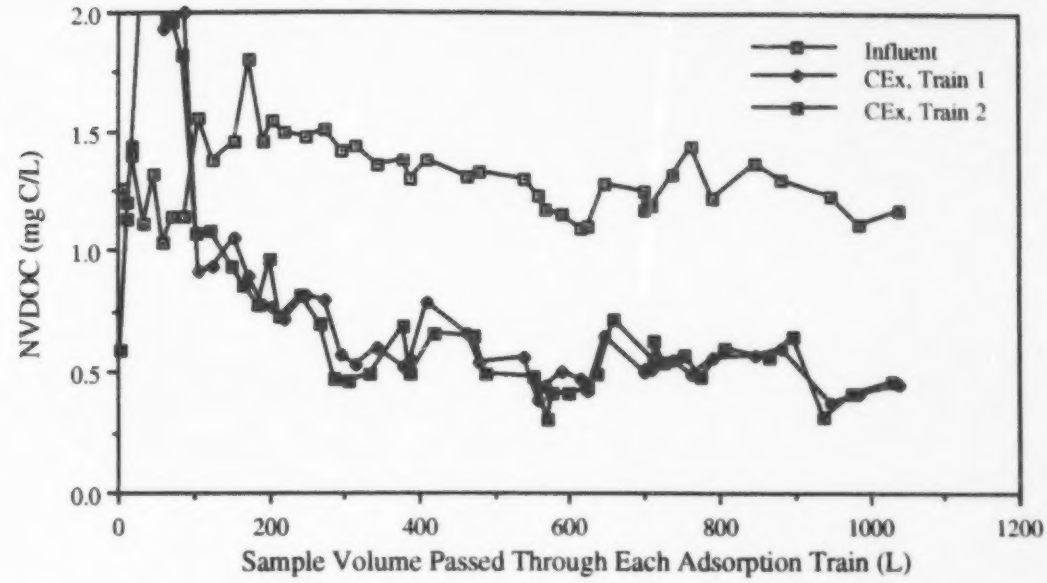


Figure II.9 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto AG MP-50 Resin

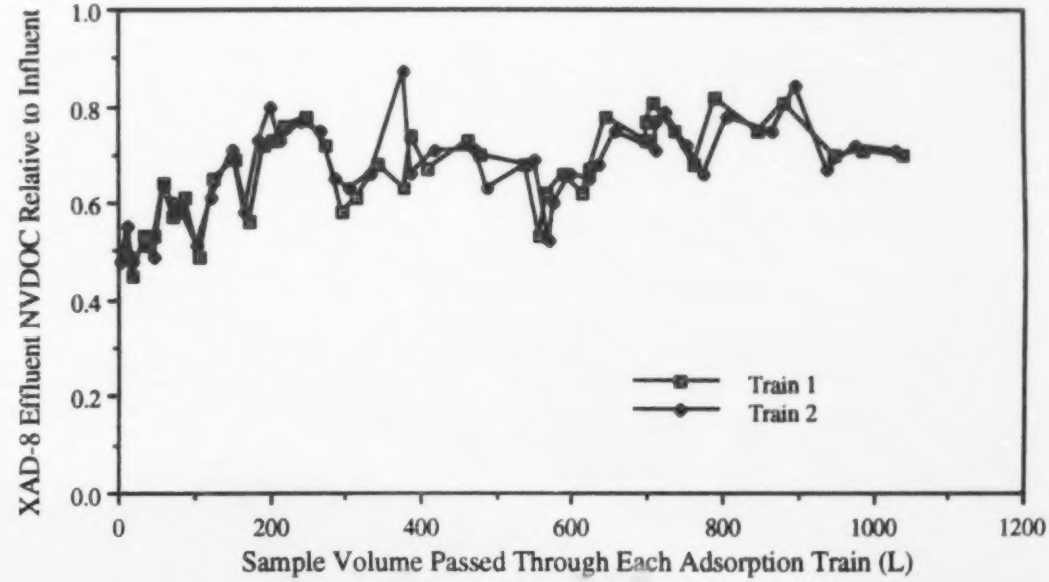


Figure II.10 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-8 Resin (Plotted Relative to Influent)

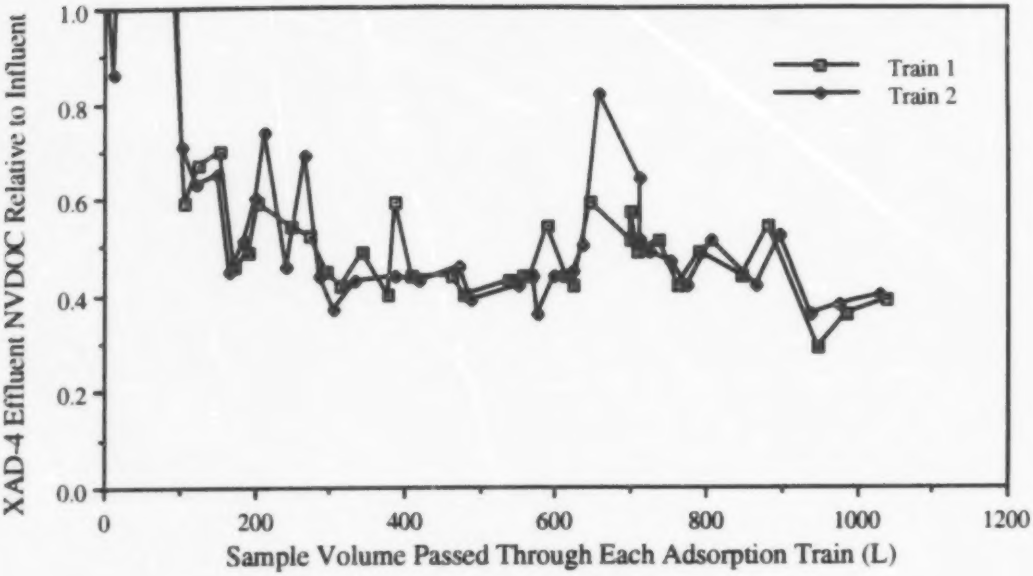


Figure II.11 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-4 Resin (Plotted Relative to Influent)

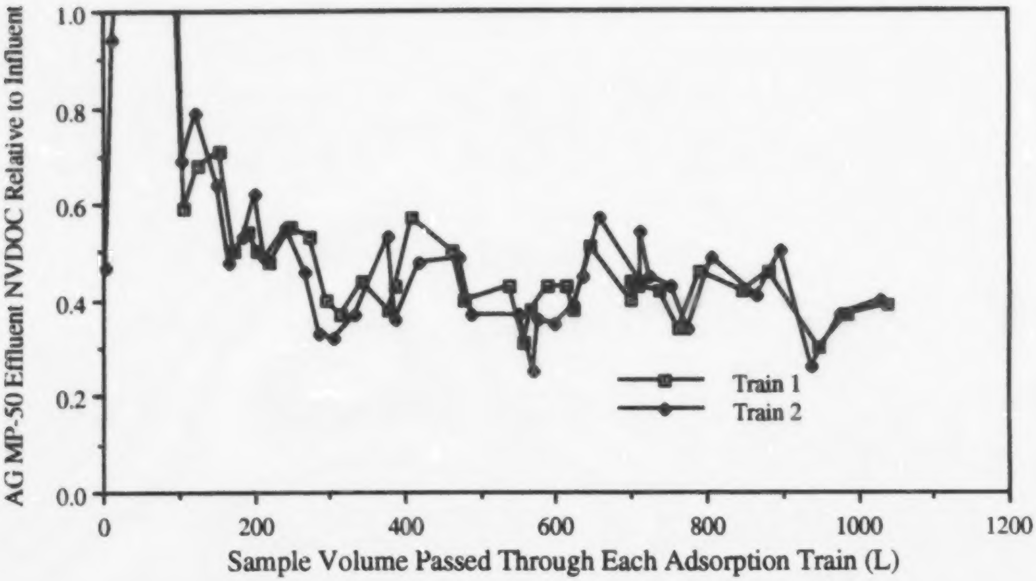


Figure II.12 NVDOC Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto AG MP-50 Resin (Plotted Relative to Influent)

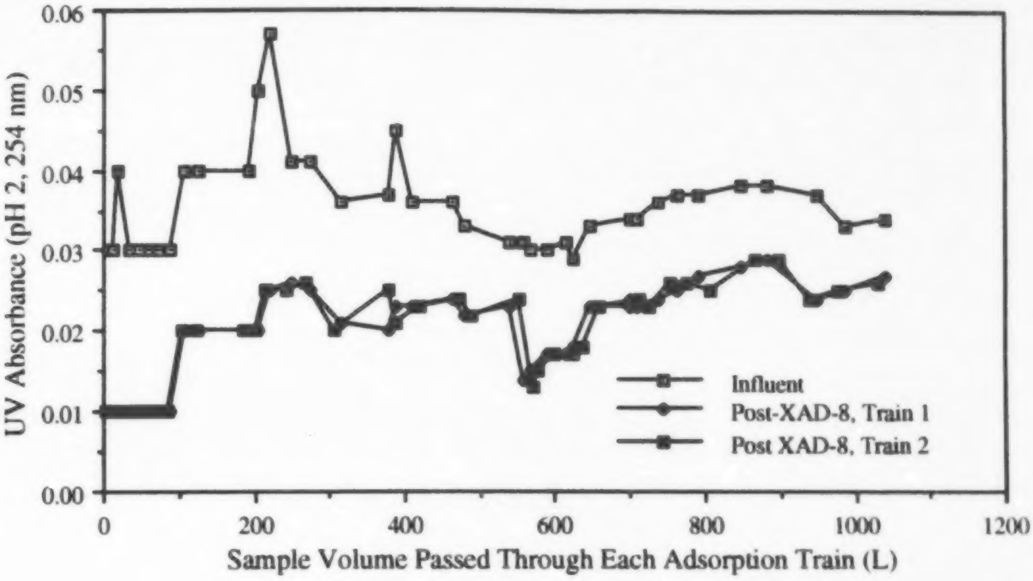


Figure II.13 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-8 Resin (pH 2, 254 nm)

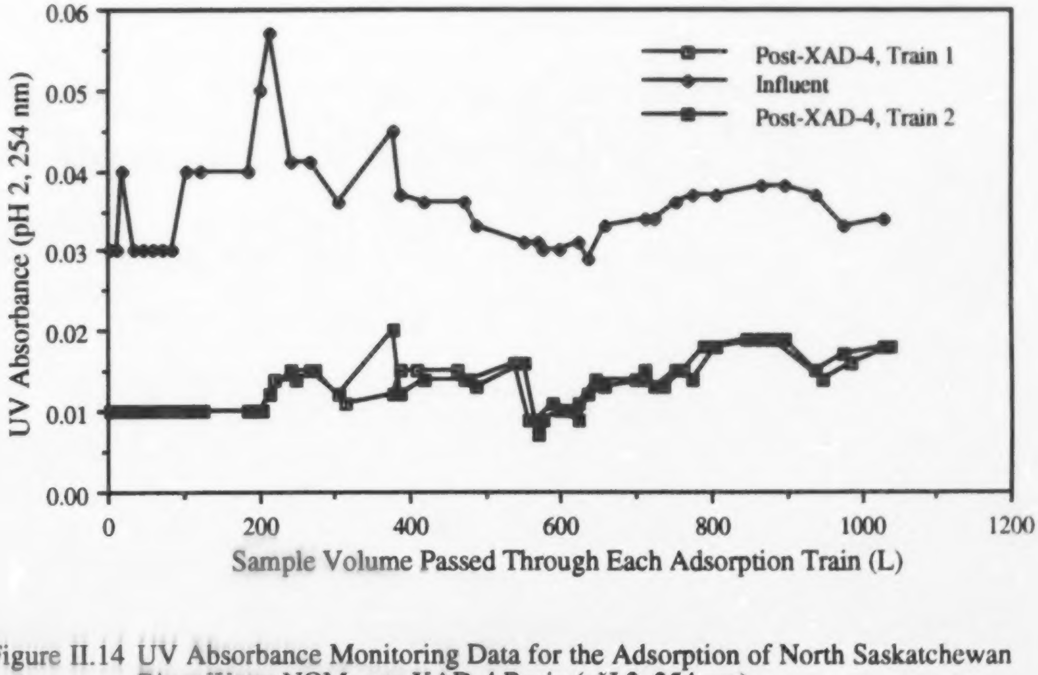


Figure II.14 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-4 Resin (pH 2, 254 nm)

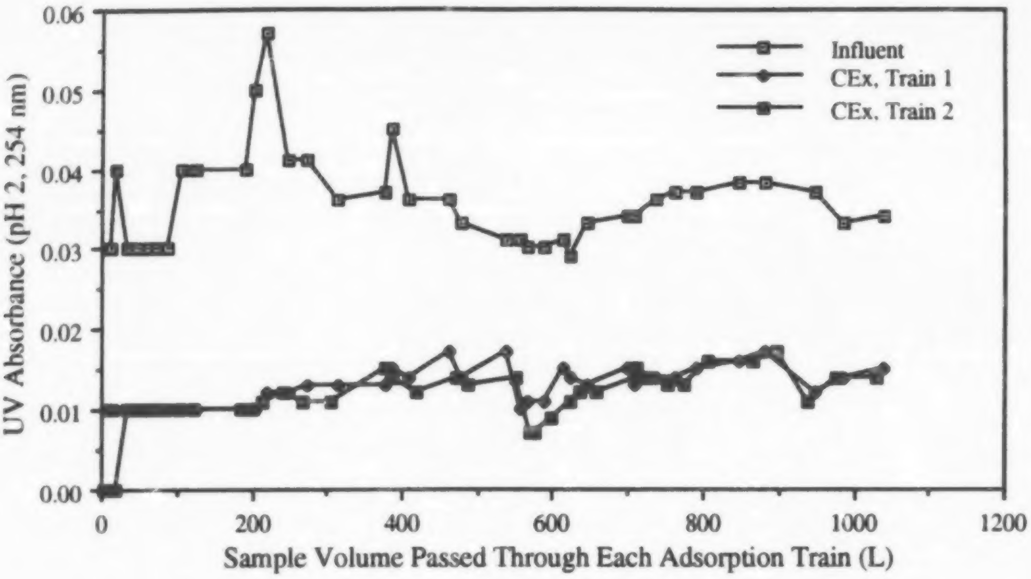


Figure II.15 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto AG MP-50 Resin (pH 2, 254 nm)

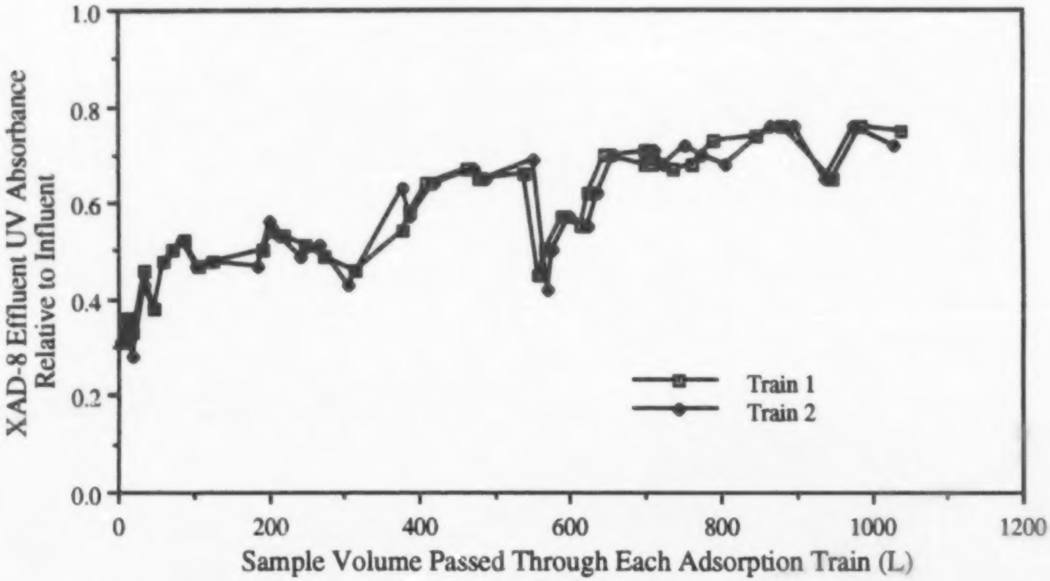


Figure II.16 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-8 Resin (Plotted Relative to Influent, pH 2, 254 nm)

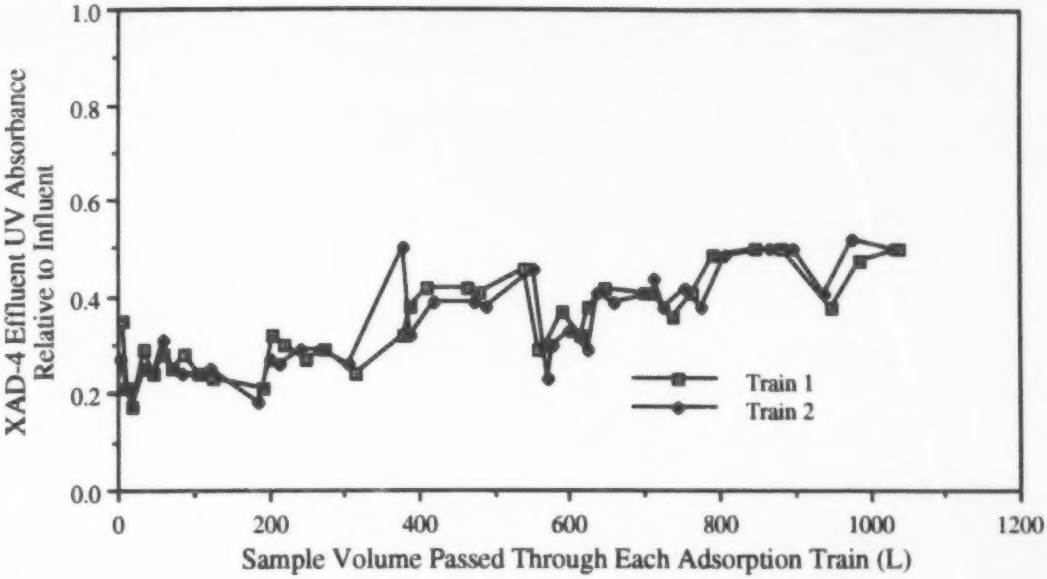


Figure II.17 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto XAD-4 Resin (Plotted Relative to Influent, pH 2, 254 nm)

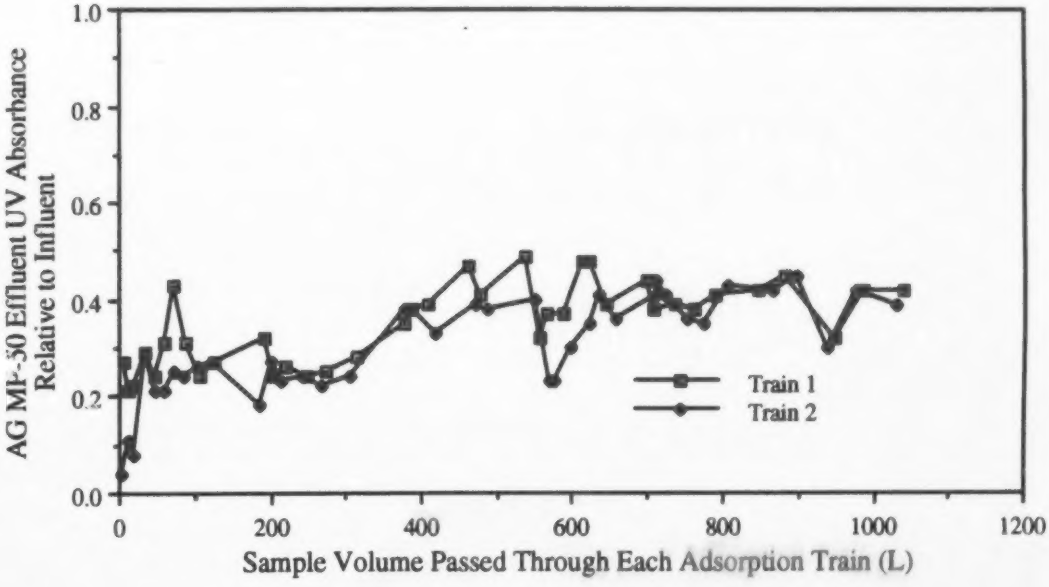


Figure II.18 UV Absorbance Monitoring Data for the Adsorption of North Saskatchewan River Water NOM onto AG MP-50 Resin (Plotted Relative to Influent, pH 2, 254 nm)

Table II.4 Typical Resin Breakthrough Data for Isolation of North Saskatchewan River and Driedmeat Lake Humics

	North Saskatchewan River				Driedmeat Lake	
	January 1992		February 1992		September 1991	
	NVDOC	UV 254nm	NVDOC	UV 254nm	NVDOC	UV 254nm
Adsorbed to XAD-8 (% of Influent)	30	51	27	34	27	44
Adsorbed to XAD-4 (% of XAD-8 Effluent)	21	47	34	38	21	50
Total Adsorption (% of Influent)	45	74	52	59	42	72
NOT Adsorbed (% of Influent)	55	26	48	41	58	28

APPENDIX III

NOM FRACTION CHARACTERIZATION DATA

This appendix contains information related to the characterization of the fractions of NOM isolated as described in Chapters 3 and 4. The UV absorbance data were collected in our laboratory, but the other information was provided by the individuals or companies listed below:

FT/IR Spectra and elemental analyses were performed at the University of Alberta Spectral Services Laboratory, University of Alberta, Edmonton, Alberta.

Molecular weight determinations were made by staff at the Alberta Research Council in Devon, Alberta.

^{13}C NMR spectra were obtained by staff in the Nuclear Magnetic Resonance Laboratory at the University of Alberta Spectral Services Laboratory, University of Alberta, Edmonton, Alberta.

Pages 267-283 are missing due to poor print quality.

APPENDIX IV

UV ABSORBANCE AND DISINFECTION BY-PRODUCTS FROM THE OZONATION OF NOM FRACTIONS AND WATER FROM DRIEDMEAT LAKE AND THE NORTH SASKATCHEWAN RIVER

This appendix contains additional data pertaining to the ozonation factorial experiments examining the effects of pH, alkalinity and ozone dosage on UV absorbance reduction and disinfection by-product (DBP) formation for the ozonation of NOM fractions and natural water samples described in Chapter 5. In particular, statistical information (confidence interval data) and sample data sheets containing the results of the individual compounds analyzed in some of the factorial experiments are included to provide the reader with this information should it be desired. Also included in this Appendix is a brief description of factorial experimental design, intended to aid the reader with no background in this area in interpreting results presented in this thesis. Further experimental protocol and results are described in Chapters 3 and 5, respectively.

The Factorial Experiment - A Brief Introduction

The factorial design enables an evaluation of the effects of several variables in a system with a minimum number of experiments by examining the variables in carefully selected combinations. In the simplest design, each of the parameters is examined at two levels, an upper level (+) and a lower level (-). For example, in the present work, the three parameters (pH, alkalinity and ozone dose) were examined at the upper and lower levels shown in Table IV.1, constituting a 2^3 factorial design (2 levels, 3 variables).

The 2^3 factorial design utilizes eight experiments defined as shown in Table IV.2. For each condition, there is another one which utilizes the same parameter levels for all parameters except one. For example in experiments 1 and 2, only the pH level is varied. By comparing the results (DBP formation, UV absorbance reduction) obtained utilizing this pair of conditions, one can determine the effect of the parameter which was different (pH in the above example). Similarly, the pH level is the only difference between experiments 3 and 4, between experiments 5 and 6, and between experiments 7 and 8. Theoretically, then, the effect of changing pH might be similar regardless of which of the above pairs of experiments is used to estimate it, and in fact an average of them might be the best estimation. In this research, the average of the halves of these pairs of experiments determined at one parameter level (for example those at pH 6) is called the 'mean effect' of the parameter at that level. The mean difference between the results obtained from the two parameter levels evaluated over the entire factorial design is called the 'main effect' of that parameter.

In addition to the experiments outlined in Table IV.2, it is advantageous to prepare replicated experiments using parameter values which are intermediate between the upper and lower levels (midpoints). The information resulting from these experiments provides the researcher with an estimate of the precision associated with the factorial experiment values, and allows quantitative estimation of the significance of differences in observed mean effects. When possible, parameter values are selected exactly midway between the upper and lower levels used, as shown in Table IV.1.

While it was not necessary in the present research, more statistical analyses may be conducted using data generated from a factorially designed experiment than that which has been discussed herein. For example, when compared differently, the experiments can also provide an indication of the extent of interaction or synergism between the parameters. For more information, the reader is directed to Box *et al.* (1978) or Davies (1979).

Table IV.1 Parameters and their Values Employed in the Factorial Design Experiments

Parameter	Level		
	-	0 (Midpoint)	+
pH	6	6.3*	8
Alkalinity (mg/L as $CaCO_3$)	0	100	200
Ozone Dose (mg:mg ozone:NVDOC)	1:1	2:1	3:1

* pH 6.3 is the midpoint hydrogen ion concentration between pH 6 and pH 8.

Table IV.2 The 2^3 Factorial Design

	Set Parameters			Determinants
Experiment	pH	Alkalinity	Ozone Dose	DBP Production
1	-	-	-	to be measured
2	+	-	-	to be measured
3	-	+	-	to be measured
4	+	+	-	to be measured
5	-	-	+	to be measured
6	+	-	+	to be measured
7	-	+	+	to be measured
8	+	+	+	to be measured

+ = upper parameter level
- = lower parameter level

Table IV.3 UV Absorbance (254 nm) Data for the Ozonation of Filtered Driedmeat Lake and North Saskatchewan River Waters

			UV Absorbance Removal (Δabs/m/mg/L NVDOC)		RAW DATA (Absorbance, 254 nm)		
			DML	NSR	DML	NSR	
NVDOC			16.35	1.68	16.35	1.68	
Initial UV Abs.(/cm/mg/L NVDOC)			0.029	0.020	0.482	0.034	pH 6
			0.030	0.021	0.497	0.036	pH 8
pH	Alkalinity	mg O3:mg C					
6	0	1	1.15	1.19	0.294	0.014	
8	0	1	1.60	1.73	0.236	0.007	
6	200	1	1.19	1.25	0.288	0.013	
8	200	1	1.52	1.73	0.248	0.007	
6	0	3	1.78	1.67	0.191	0.006	
8	0	3	1.92	2.14	0.183	0.000	
6	200	3	1.82	1.73	0.185	0.005	
8	200	3	2.02	2.14	0.167	0.000	
6.3	100	2	1.66	1.67	0.211	0.006	
6.3	100	2	1.71	1.79	0.218	0.006	
6.3	100	2	1.58	1.73	0.223	0.005	
Ozonation of Natural Water			1.80	1.67	0.203	0.008	

Main Effects (Δabs/m/mg/L NVDOC)	pH	0.281	0.476
	Alkalinity	0.024	0.030
	mg O3: mg C	0.520	0.446
	Factorial Average	1.62	1.70
	Midpoint RSD (%)	3.73	3.45

Two Level Interactions	1,2	-0.012	-0.030
	1,3	-0.110	-0.030
	2,3	0.171	0.000

		DML	NSR
Mean UV Reductions (Δabs/m/mg/L NVDOC)	pH 6	1.48	1.46
	pH 8	1.76	1.93
	0 alk	1.61	1.68
	200 alk	1.64	1.71
	1 to 1	1.36	1.47
	3 to 1	1.88	1.92

* 10 minute post-ozone reaction time employed

Table IV.4 UV Absorbance (270 nm) Data for the Ozonation of Filtered Driedmeat Lake and North Saskatchewan River Waters

			UV Absorbance Removal (Δabs/m/mg/L NVDOC)		RAW DATA (Absorbance, 270 nm)		
			DML	NSR	DML	NSR	
NVDOC			16.35	1.68	16.35	1.68	
Initial UV Abs.(/cm/mg/L NVDOC)			0.022	0.017	0.359	0.029	pH 6
			0.023	0.018	0.381	0.031	pH 8
pH	Alkalinity	mg O3:mg C					
6	0	1	0.813	1.07	0.226	0.011	
8	0	1	1.24	1.61	0.179	0.004	
6	200	1	0.844	1.13	0.221	0.010	
8	200	1	1.18	1.55	0.188	0.005	
6	0	3	1.30	1.49	0.146	0.004	
8	0	3	1.46	1.85	0.143	0.000	
6	200	3	1.32	1.55	0.143	0.003	
8	200	3	1.54	1.85	0.129	0.000	
6.3	100	2	1.20	1.49	0.162	0.004	
6.3	100	2	1.31	1.61	0.167	0.004	
6.3	100	2	1.14	1.55	0.172	0.003	
Ozonation of Natural Water			1.38	1.49	0.155	0.006	

Main Effects (Δabs/m/mg/L NVDOC)	pH	0.283	0.402
	Alkalinity	0.020	0.015
	mg O3:mg C	0.387	0.342
	Factorial Average	1.21	1.51
	Midpoint RSD (%)	6.85	3.85

Two Level Interactions	1,2	-0.005	-0.045
	1,3	-0.096	-0.074
	2,3	0.128	0.060

		DML	NSR
MeanUV Reductions (Δabs/m/mg/L NVDOC)	pH 6	1.07	1.31
	pH 8	1.35	1.71
	0 alk	1.20	1.50
	200 alk	1.22	1.52
	1 to 1	1.02	1.34
	3 to 1	1.41	1.68

* 10 minute post-ozone reaction time employed

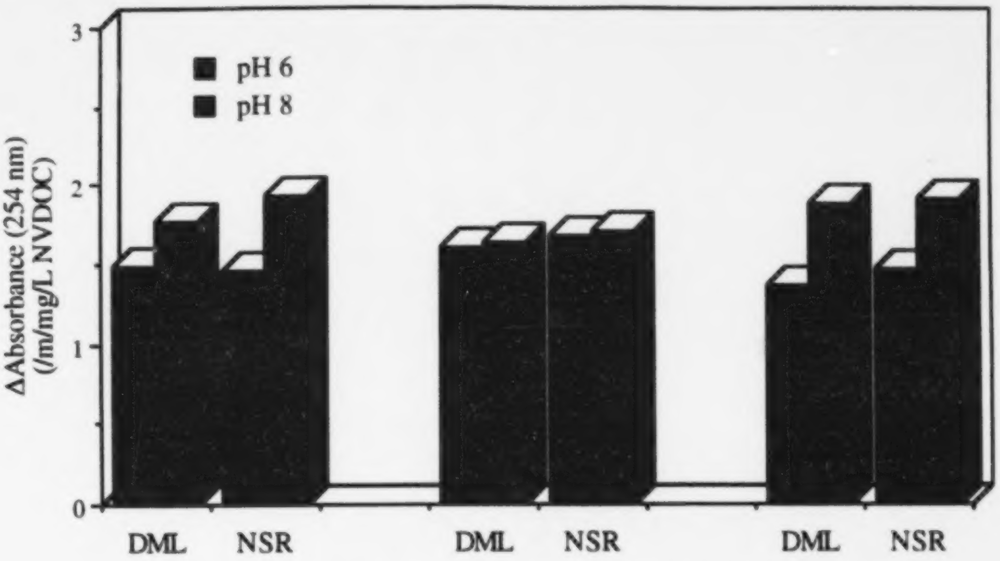


Figure IV.1 Effects of pH, Alkalinity and Ozone Dose on UV Absorbance Reductions for Two Natural Waters (DML = Driedmeat Lake, NSR = North Saskatchewan River, 254 nm)

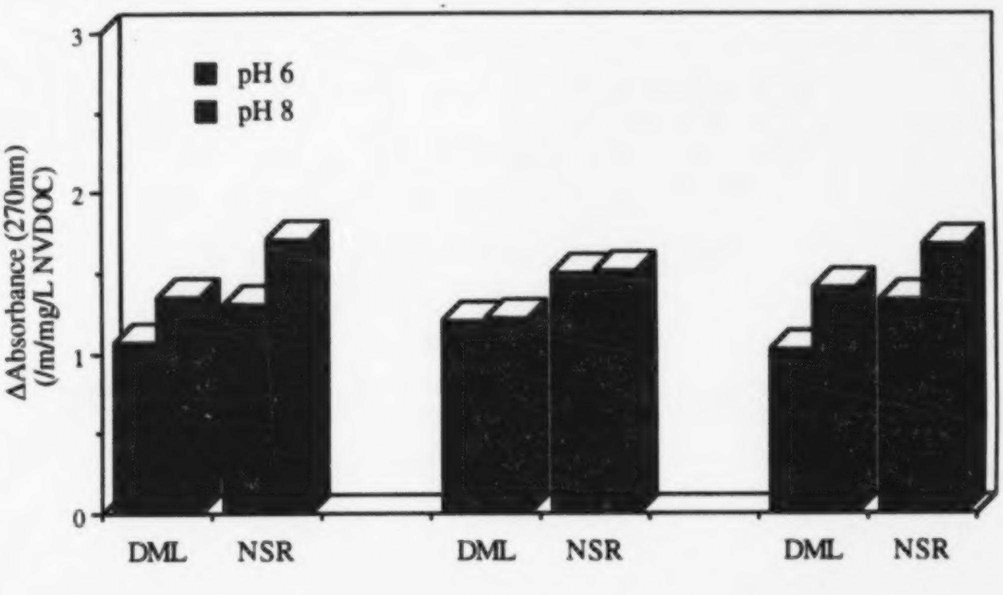


Figure IV.2 Effects of pH, Alkalinity and Ozone Dose on UV Absorbance Reductions for Two Natural Waters (DML = Driedmeat Lake, NSR = North Saskatchewan River, 270 nm)

Table IV.5 Confidence Intervals for Ozonation Factorials - UV Absorbance Data for Ozonation of Fulvic Acid Fractions at 20 mg/L NVDOC

	IHSS	DML8	NSR8	NSR4
Standard Deviation (s)*	0.258	0.219	0.509	0.140
95% CI	0.365	0.309	0.720	0.198
RCI	1.21%	1.04%	2.33%	1.19%
90% CI	0.215	0.182	0.423	0.116
RCI	0.67%	0.56%	1.28%	0.68%

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.6 Confidence Intervals for Ozonation Factorials - UV Absorbance Data for Ozonation of Fulvic Acid Fractions at 5 mg/L NVDOC

	254 nm				270 nm			
	DML8	DML4	NSR8	NSR4	DML8	DML4	NSR8	NSR4
Standard Deviation (s)*	0.080	0.076	0.136	0.042	0.080	0.042	0.167	0.035
95% CI	0.113	0.107	0.193	0.059	0.113	0.059	0.236	0.049
RCI	6.8%	9.3%	9.7%	3.6%	8.2%	5.7%	13%	3.7%
90% CI	0.067	0.063	0.113	0.035	0.067	0.035	0.138	0.029
RCI	4.0%	5.5%	5.7%	2.1%	4.8%	3.3%	8.1%	2.2%

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.7 Confidence Intervals for Ozonation Factorials - UV Absorbance Data for Ozonation of Filtered Raw Waters

	254 nm		270 nm	
	DML	NSR	DML	NSR
Standard Deviation (s)*	0.062	0.060	0.083	0.060
95% CI	0.087	0.084	0.118	0.084
RCI	5.4%	5.0%	9.7%	5.6%
90% CI	0.051	0.049	0.069	0.049
RCI	3.2%	2.9%	5.7%	3.3%

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.8 Confidence Intervals for Ozonation Factorials - Aldehyde Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
20 mg/L NVDOC					
IHSS	53.0	75.5	4.11	44.4	2.10
DML8	36.9	52.3	4.43	30.7	2.56
NSR8	65.3	92.4	8.89	54.3	5.24
NSR4	113	159	12.1	93.5	7.14
5 mg/L NVDOC					
DML8	112	158	4.56	93.1	2.74
DML4	268	379	6.02	223	3.55
NSR8	305	432	11.9	254	7.02
NSR4	359	507	9.04	298	5.23
Filtered Raw					
DML	38.4	54.3	7.56	31.9	4.45
NSR	153	217	10.0	127	5.89

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.9 Confidence Intervals for Ozonation Factorials - Oxoacid Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
20 mg/L NVDOC					
IHSS	1.44	2.03	1.89	1.24	1.01
DML8	2.81	4.04	1.36	2.34	0.94
NSR8	4.97	7.10	8.38	4.17	4.89
NSR4	8.56	12.2	15.2	7.11	9.03
5 mg/L NVDOC					
DML8	5.71	7.98	3.45	4.67	2.04
DML4	23.0	32.5	10.5	19.1	6.21
NSR8	70.0	98.0	47.0	58.0	28.0
NSR4	20.4	28.8	13.8	16.9	8.15
Filtered Raw					
DML	18.0	25.5	7.22	15.0	4.22
NSR	17.7	25.1	2.73	14.8	1.61

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.10 Confidence Intervals for Ozonation Factorials - Carboxylic Acid Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
20 mg/L NVDOC					
IHSS	12.2	17.2	4.04	10.1	2.33
DML8	24.8	35.1	6.24	20.6	3.67
NSR8	23.3	33.0	8.78	19.4	5.25
NSR4	36.2	51.2	15.7	30.1	9.24
5 mg/L NVDOC					
DML8	49.0	69.4	10.1	40.8	5.89
DML4	189	268	20.6	157	12.1
NSR8	19.0	27.3	10.9	16.0	6.43
NSR4	9.93	14.1	9.00	8.29	5.31
Filtered Raw					
DML	42.1	59.6	16.8	35.0	9.78
NSR	149	204	22.1	120	13.0

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River; IHSS = International Humic Substances Society; 8/4 = XAD-8 or XAD-4 resin concentrate

Table IV.11 Statistics Relating to UV-Oxoacid Correlations

Fraction	r^2	r	Z	z	Significance (95%)	Significance (90%)
5 mg/L NVDOC						
DML8	0.954	0.977	2.23	3.86	+	+
DML4	0.998	0.999	3.80	6.58	+	+
NSR8	0.430	0.656	0.786	1.36	-	-
NSR4	0.990	0.994	2.90	5.02	+	+
20 mg/L NVDOC						
IHSS	0.366	0.605	0.701	1.21	-	-
DML8	0.419	0.647	0.770	1.33	-	-
NSR8	0.040	0.200	0.203	0.35	-	-
NSR4	0.389	0.624	0.732	1.27	-	-

$$Z = 0.5 \ln \frac{1+r}{1-r}$$

$$z = \sqrt{n-3}\, Z$$

$z_{(\alpha/2=0.025)} = 1.96$
$z_{(\alpha/2=0.050)} = 1.66$

Table IV.12 Fulvic Acids Ozonation Factorials - Ozone Residuals Data

20 mg/L NVDOC			OZONE RESIDUAL (mg/L)				RAW DATA (ABSORBANCE, 600 nm)			
			IHSS	DML	NSR	NSR	IHSS	DML	NSR	NSR
pH	Alkalinity	mg O3 : mg C	(XAD-8)	(XAD-8)	(XAD-8)	(XAD-4)	(XAD-8)	(XAD-8)	(XAD-8)	(XAD-4)
6	0	1	2.62	2.62	6.67	8.33	0.189	0.189	0.172	0.165
8	0	1	0.714	0.714	2.14	2.14	0.197	0.197	0.191	0.191
6	200	1	0.952	3.57	4.52	5.24	0.196	0.185	0.181	0.178
8	200	1	0.952	1.19	1.19	1.67	0.196	0.195	0.195	0.193
6	0	3	5.00	10.5	11.0	17.6	0.179	0.156	0.154	0.126
8	0	3	1.43	1.19	2.14	0.952	0.194	0.195	0.191	0.196
6	200	3	2.14	7.14	13.3	14.0	0.191	0.170	0.144	0.141
8	200	3	0.714	0.952	4.76	0.952	0.197	0.196	0.180	0.196

Main Effect:	pH	-1.73	-4.94	-6.31	-9.88
(mg O3/L)	Alkalinity	-1.25	-0.54	0.48	-1.79
	mg O3: mg C	1.01	2.92	4.17	4.05
	Average	1.82	3.48	5.71	6.37

Level Interactions	1,2	1.01	0.65	0.36	1.55
(mg O3/L)	1,3	-0.77	-2.80	-2.38	-5.00
	2,3	-2.14	-5.00	8.10	0.00

		IHSS (XAD-8)	DML (XAD-8)	NSR (XAD-8)	NSR (XAD-4)
Mean Effects					
(mg O3/L)	pH 6	2.68	5.95	8.87	11.3
	pH 8	0.952	1.01	2.56	1.43
	0 Alk	2.44	3.75	5.48	7.26
	200 Alk	1.19	3.21	5.95	5.48
	1:1	1.31	2.02	3.63	4.35
	3:1	2.32	4.94	7.80	8.39

Table IV.13 DML Filtered Raw Water Ozonation Factorial - Raw Data

NVDOC: 16.35 mgC/L
10 min post-ozonation reaction time

DBP and I.S. Peak Area Counts x 10^5

pH	Added Alk.	O3:C (mg:mg)	DBP I.S.	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomalonic Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
6	0	1	4.83	159	46.9	18.5	11.9	108	67.7	9.70	20.9	0.140	0.798	0.121	0.850	0.0155
8	0	1	5.01	149	42.9	13.5	5.63	110	61.1	16.5	38.2	0.145	0.791	0.161	1.88	0.0491
6	200	1	4.44	160	44.6	16.0	11.5	100	67.2	10.9	17.6	0.320	0.800	0.159	0.950	0.0128
8	200	1	4.74	143	39.7	15.4	5.79	111	63.9	5.00	40.8	0.252	0.579	0.152	0.930	0.0378
6	0	3	4.52	211	48.8	32.5	24.5	198	179	13.4	69.2	0.451	0.958	0.145	1.27	0.0359
8	0	3	4.85	199	42.4	35.9	9.94	193	123	17.1	106	0.431	0.951	0.259	1.97	0.0908
6	200	3	4.21	252	50.5	29.1	22.4	197	165	11.7	59.1	0.484	1.36	0.215	0.870	0.0358
8	200	3	5.14	205	43.2	36.2	8.12	213	151	15.8	114	0.354	1.26	0.201	0.850	0.0611
6.3	100	2	4.57	186	46.9	29.9	16.1	185	115	18.0	70.9	0.275	0.963	0.171	1.80	0.0303
6.3	100	2	5.31	177	51.3	31.3	15.1	192	136	17.8	76.2	0.241	1.07	0.213	1.92	0.0295
6.3	100	2	4.72	169	48.6	27.9	15.6	177	130	18.1	66.4	0.224	1.00	0.201	1.53	0.0325
Standard			4.58	420	236	27.0	LDL	10.4	38.8	50.1	4.00	0.131	1.13	3.51	1.98	10.1
Blank			4.27	47.5	40.0	0.365	LDL	0.280	0.619	1.08	0.167	0.0623	0.268	0.175	1.83	0.0580
DML Spike			4.57	432	247	29.5	LDL	12.1	42.3	52.5	4.66	0.138	1.30	3.81	2.08	10.3
DML no ozone			4.57	50.1	38.1	0.625	0.216	1.61	2.10	3.63	0.315	0.0713	0.404	0.200	1.39	0.0188
RAW (O3 Nat 3:1)			3.96	182	41.8	33.2	12.2	181	155	13.3	52.7	0.223	0.590	0.136	1.82	0.0220

		DBP I.S.	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomalonic Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
Main Effects	pH	0.44	-21.5	-5.7	1.2	-10.2	6.0	-20	2.2	33.1	-0.053	-0.084	0.033	NA	0.035
	Alkalinity	-0.17	10.5	-0.8	-0.9	-1.0	3.0	4	-3.3	-0.7	0.061	0.125	0.010	NA	-0.011
	mg O3: mg C	-0.08	64.0	2.7	17.6	7.5	93	90	4.0	57.7	0.216	0.390	0.057	NA	0.027
	Average	4.76	183	46.0	26.0	13.3	162	114	14.0	61.8	0.302	0.957	0.182	NA	0.039
RSD of Midpoints (%)		8.0	4.8	4.5	5.8	3.2	4.1	8.5	0.9	6.9	10.5	5.4	11.1	11.4	5.0
Two Level	1,2	NA	-11	-0.5	2.0	0.2	8	11	-3.1	6.0	-0.046	-0.077	-0.044	NA	-0.010
Interactions	1,3	NA	-8	-1.2	4.0	-4.2	-1	-15	1.7	12.8	-0.022	0.030	0.017	NA	0.005
	2,3	NA	52	8.0	-2.5	-3.7	26	12	7.3	-1.4	-0.331	0.921	-0.017	NA	-0.016

LDL = Less than Detection Limit NA = Not Applicable

	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomalonic Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
Nominal Conc. (µg/L)	802	394	50	NA	15	35	241	NA	211	339	295	NA	372
Standard	807	342	53.5	NA	14.4	31.5	245	NA	212	350	302	NA	338
Blank	3	15	0.5	LDL	0.4	0.5	5.3	0.5	27	7	1.7	NA	9.1
DML Spike	833	360	58.5	NA	16.7	34.3	257	NA	231	418	329	NA	344
DML no ozone	8	12	1.0	0.3	2.2	1.7	17.8	1.0	51	61	13.9	NA	7.9

Table IV.14 DML Filtered Raw Water Ozonation Factorial - µg/mg NVDOC Concentrations

NVDOC: 16.35 mgC/L
10 min post-ozonation reaction time

Concentration (µg DBP/mg NVDOC)

pH	Added Alk.	O3:C (mg:mg)	DBP I.S.	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomalonic Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
6	0	1	NA	14.9	1.61	2.24	1.35	9.12	3.36	2.91	4.06	14.5	13.3	0.431	NA	0.474
8	0	1	NA	13.6	1.20	1.63	0.64	9.28	3.03	4.94	7.43	21.4	13.1	0.644	NA	0.541
6	200	1	NA	15.0	1.38	1.94	1.31	8.44	3.33	3.27	3.42	44.2	13.4	0.633	NA	0.468
8	200	1	NA	12.8	0.87	1.86	0.66	9.37	3.17	1.50	7.94	39.1	7.98	0.596	NA	0.518
6	0	3	NA	21.8	1.80	3.94	2.80	16.7	8.88	4.02	13.5	65.9	17.2	0.558	NA	0.515
8	0	3	NA	20.2	1.15	4.36	1.13	16.3	6.10	5.12	20.6	68.7	17.0	1.17	NA	0.624
6	200	3	NA	27.2	1.98	3.53	2.56	16.6	8.18	3.51	11.5	71.4	27.0	0.931	NA	0.514
8	200	3	NA	21.0	1.23	4.39	0.92	18.0	7.49	4.74	22.2	56.0	24.6	0.857	NA	0.565
6.3	100	2	NA	18.5	1.61	3.63	1.84	15.6	5.70	5.39	13.8	36.8	17.3	0.697	NA	0.503
6.3	100	2	NA	17.3	2.06	3.80	1.72	16.2	6.75	5.33	14.8	31.2	19.9	0.921	NA	0.502
6.3	100	2	NA	16.2	1.78	3.38	1.78	14.9	6.45	5.42	12.9	28.4	18.2	0.857	NA	0.508
Main Effects		pH	NA	-2.8	-0.58	0.15	-1.17	0.51	-0.99	0.65	6.43	-2.7	-2.0	0.177	NA	0.069
		Alkalinity	NA	1.4	-0.08	-0.11	-0.12	0.25	0.20	-1.00	-0.14	10.0	3.0	0.055	NA	-0.022
		mg O3: mg C	NA	8.5	0.28	2.14	0.86	7.85	4.44	1.19	11.2	35.7	9.5	0.302	NA	0.054
		Average	NA	18.0	1.52	3.15	1.52	13.7	5.68	4.20	12.0	43.4	17.2	0.754	NA	0.521
Two Level Interactions		1,2	NA	-1.4	-0.05	0.25	0.02	0.6	0.56	-0.92	1.17	-7.6	-1.9	-0.233	NA	-0.019
		1,3	NA	-1.1	-0.12	0.49	-0.48	0.0	-0.75	0.52	2.49	-3.6	0.7	0.089	NA	0.011
		2,3	NA	6.9	0.82	-0.30	-0.42	2.2	0.58	2.19	-0.27	-54.7	22.4	-0.091	NA	-0.032

NA - Not Applicable

Table IV.15 DML Filtered Raw Water Ozonation Factorial - µmol/g NVDOC Concentrations

NVDOC: 16.35 mgC/L
10 min post-ozonation reaction time

Concentration (µmol DBP/g NVDOC)

pH	Added Alk.	O3:C (mg:mg)	DBP I.S.	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomalonic Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
6	0	1	NA	496	36.6	38.6	18.8	123	38.2	24.6	30.8	315	222	5.82	NA	4.47
8	0	1	NA	452	27.3	28.1	8.86	125	34.4	41.9	56.3	465	219	8.70	NA	5.10
6	200	1	NA	501	31.3	33.4	18.2	114	37.9	27.7	25.9	962	223	8.55	NA	4.42
8	200	1	NA	426	19.9	32.1	9.11	127	36.0	12.7	60.1	850	133	8.05	NA	4.89
6	0	3	NA	725	41.0	68.0	38.8	226	101	34.0	102	1430	287	7.55	NA	4.85
8	0	3	NA	672	26.1	75.1	15.7	220	69.3	43.4	156	1490	284	15.8	NA	5.89
6	200	3	NA	906	44.9	60.9	35.5	225	93.0	29.7	87.1	1550	450	12.6	NA	4.85
8	200	3	NA	699	28.0	75.8	12.8	243	85.1	40.1	168	1220	409	11.6	NA	5.33
6.3	100	2	NA	615	36.6	62.5	25.5	211	64.8	45.7	104	800	289	9.42	NA	4.75
6.3	100	2	NA	576	46.8	65.5	23.9	219	76.7	45.2	112	678	332	12.4	NA	4.73
6.3	100	2	NA	540	40.5	58.3	24.7	202	73.3	46.0	97.8	617	304	12.4	NA	4.73
Main Effects		pH	NA	-95	-13.1	2.6	-16.2	6.8	-11.3	5.5	48.7	-58	-34	2.39	NA	0.65
		Alkalinity	NA	46	-1.7	-1.9	-1.7	3.4	2.3	-8.4	-1.0	220	51	0.74	NA	-0.21
		mg O3: mg C	NA	282	6.3	36.9	12.0	106	50.5	10.1	85.0	775	158	4.09	NA	0.51
		Average	NA	601	34.5	54.4	21.1	185	64.5	35.6	91.0	943	286	10.26	NA	4.91
Two Level Interactions		1,2	NA	-46	-1.0	4.2	0.3	9	6.4	-7.8	8.8	-163	-31	-3.15	NA	-0.18
		1,3	NA	-35	-2.8	8.4	-6.7	-1	-8.5	4.4	18.9	-77	12	1.21	NA	0.10
		2,3	NA	229	18.6	-5.2	-5.8	30	6.6	18.5	-2.1	-1182	374	-1.22	NA	-0.30

*NA = Not Applicable

Mean Effects		
Total aldehydes	pH 6	774
	pH 8	652
	0 alk	692
	200 alk	733
	1 to 1	542
	3 to 1	881
Total oxoacids	pH 6	330
	pH 8	380
	0 alk	357
	200 alk	353
	1 to 1	229
	3 to 1	481
Carboxylic acids	pH 6	1359
	pH 8	1268
	0 alk	1178
	200 alk	1449
	1 to 1	847
	3 to 1	1780

Table IV.16 NSR Filtered Raw Water Ozonation Factorial - µmol/g NVDOC Concentrations

NVDOC: 1.67 mgC/L
10 min post-ozonation reaction time

Concentration (µmol DBP/g NVDOC)

pH	Added Alk.	O3:C (mg:mg)	DBP I.S.	Formald.	Acetald.	Glyoxal	Methyl Glyoxal	Glyoxylic Acid	Pyruvic Acid	Ketomaloni Acid	Oxalacetic Acid	Formic Acid	Acetic Acid	Propanoic Acid	MBA I.S.	Benzoic Acid
6	0	1	NA	2251	680	249	113	166	136	62.4	16.6	1020	3808	92.1	NA	45.5
8	0	1	NA	914	355	269	201	145	49.1	75.1	54.7	111	2172	79.7	NA	32.2
6	200	1	NA	1380	466	110	53.3	160	28.8	56.9	17.2	340	2295	69.6	NA	15.6
8	200	1	NA	1522	450	267	129	140	24.8	76.3	44.1	682	2704	85.5	NA	39.6
6	0	3	NA	1638	530	302	127	212	64.0	125	18.2	611	1683	58.0	NA	15.5
8	0	3	NA	1794	559	281	164	204	53.6	168	70.8	132	5079	85.5	NA	52.7
6	200	3	NA	1664	555	81.1	131	112	67.3	108	33.2	1245	3729	135	NA	14.4
8	200	3	NA	2134	591	382	138	200	40.4	183	27.0	699	2303	79.7	NA	48.0
6.3	100	2	NA	1018	439	290	158	188	33.1	136	47.5	495	3808	101	NA	57.8
6.3	100	2	NA	1207	500	314	146	180	34.5	118	50.6	453	3332	125	NA	42.2
6.3	100	2	NA	1255	475	288	153	171	31.3	122	45.2	541	3284	101	NA	33.0
Main Effects		pH	NA	-142	-69	114	52	10	-32.0	37.6	27.9	-398	186	-6.0	NA	20.4
		Alkalinity	NA	26	-15	-65	-39	-29	-35.3	-1.7	-9.7	273	-428	13.6	NA	-7.1
		mg O3: mg C	NA	291	71	38	16	29	-3.3	78.1	4.1	134	454	7.8	NA	-0.6
		Average	NA	1525	509	258	138	171	51.1	112	38.6	575	3109	92.0	NA	36.0
Two Level		1,2	NA	448	79	114	-11	24	16.6	9.6	-17.5	296	-694	-13.6	NA	8.4
Interactions		1,3	NA	455	102	26	-30	30	13.3	21.6	-4.7	-114	799	-7.8	NA	15.0
		2,3	NA	629	175	20	111	-93	121	1.7	-18.9	1309	250	87.7	NA	16.6

Mean Effects	Total aldehydes	pH 6	2583
		pH 8	2538
		0 alk	2607
		200 alk	2514
		1 to 1	2271
		3 to 1	2768
	Total oxoacids	pH 6	346
		pH 8	389
		0 alk	405
		200 alk	329
		1 to 1	313
		3 to 1	421
	Carboxylic acids	pH 6	3683
		pH 8	3471
		0 alk	3654
		200 alk	3499
		1 to 1	3283
		3 to 1	3870

* NA = Not Applicable

APPENDIX V

EFFECT OF NVDOC CONCENTRATION ON ORGANIC OZONATION BY-PRODUCT FORMATION (DATA AT PH 8)

An experiment was conducted to evaluate the effect of NVDOC concentration on DBP formation at constant ozone to NVDOC ratio. Using lakewater fulvic acids isolated on XAD-8 resin, NVDOC concentrations of 2.5, 5, 10 and 20 mgC/L were ozonated at a 3:1 ozone to NVDOC ratio at pH 6 and 8 and without additional alkalinity. Ozonation DBPs, ozone residual and UV reduction were measured. Data collected at pH 6 were reported in Chapter 6, data collected at pH 8 (and not in Chapter 6) are reported herein.

The effect of varying NVDOC concentrations on formaldehyde and acetaldehyde yields at pH 8 and a constant ozone:NVDOC ratio is illustrated in Figure V.1 and is typical of the results obtained for most of the ozonation DBPs studied. For completeness, similar effects for other DBPs at pH 8 are shown in Figures V.2 to V.4.

The data reported here for pH 8 agree with those reported at pH 6 (except for glyoxal and methyl glyoxal), which are discussed in Chapter 6.

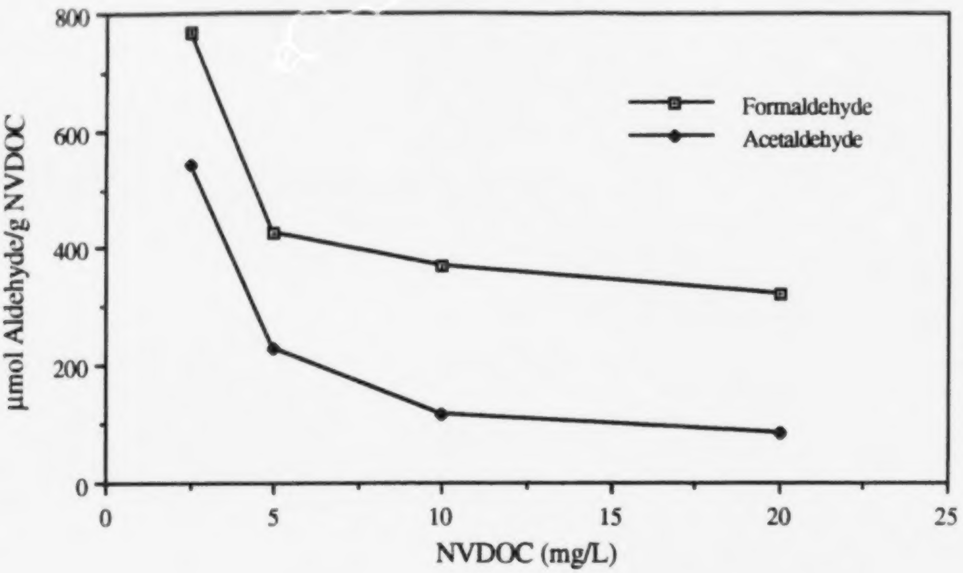


Figure V.1 Effect of NVDOC Concentration on Formaldehyde and Acetaldehyde Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 8, No Added Alkalinity.

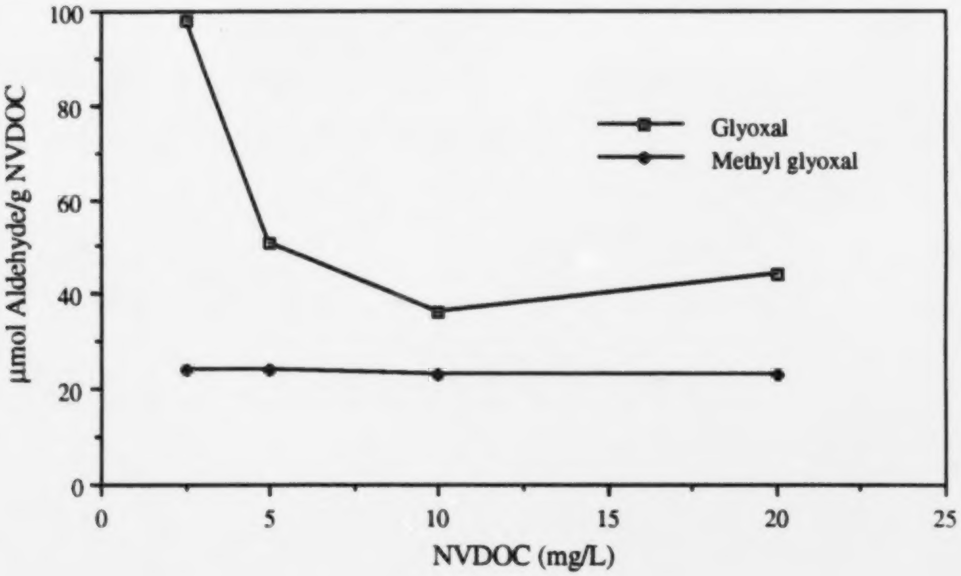


Figure V.2 Effect of NVDOC Concentration on Glyoxal and Methyl Glyoxal Formation at a Constant Ozone:NVDOC Ratio of 3:1, pH 8, No Added Alkalinity.

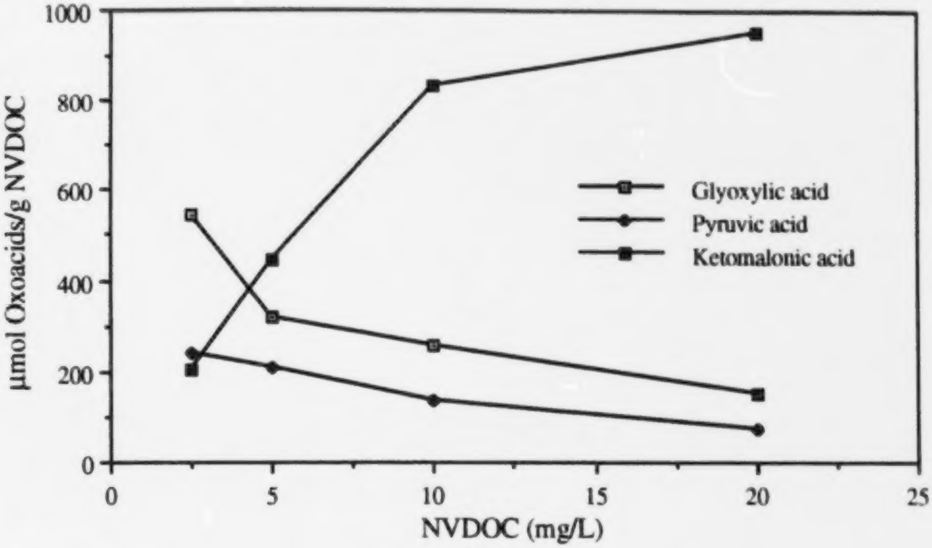


Figure V.3 Effect of NVDOC Concentration on Oxoacid Formation on at a Constant Ozone:NVDOC Ratio of 3:1, pH 8, No Added Alkalinity.

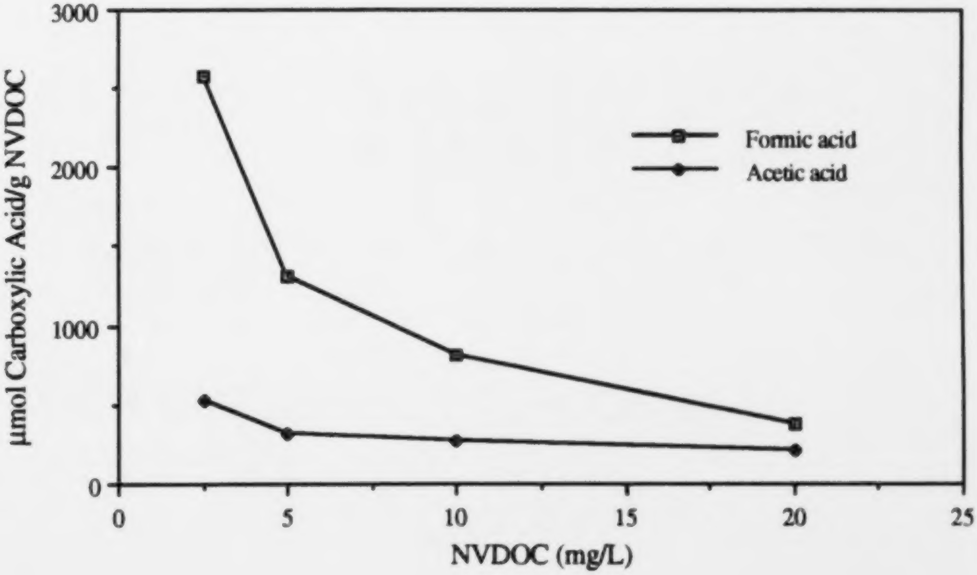


Figure V.4 Effect of NVDOC Concentration on Carboxylic Acid Formation on at a Constant Ozone:NVDOC Ratio of 3:1, pH 8, No Added Alkalinity.

APPENDIX VI

HALOGENATED DISINFECTION BY-PRODUCTS FROM OZONATION AND CHLORINATION OF ISOLATED NOM AND OF WATER FROM DRIEDMEAT LAKE AND THE NORTH SASKATCHEWAN RIVER

This appendix contains additional data pertaining to the factorial experiments examining the effects of pH, alkalinity and ozone dosage on subsequent halogenated disinfection by-product (XDBP) formation for the natural water samples described in Chapter 7.1. Samples were obtained from Driedmeat Lake and the North Saskatchewan River (NVDOC 16.35 and 1.67 mgC/L, respectively). Selected samples were first ozonated at a 1:1 or 3:1 applied ozone:NVDOC ratio, at pH 6 or 8, and either without additional alkalinity or with 200 mg/L as $CaCO_3$ added alkalinity (added as $NaHCO_3$). All were chlorinated at a 3:1 Cl_2:NVDOC ratio using reagent grade sodium hypochlorite under the same pH and alkalinity conditions mentioned above. XDBPs measured included the trihalomethanes, haloacetic acids, chloral hydrate and cyanogen chloride.

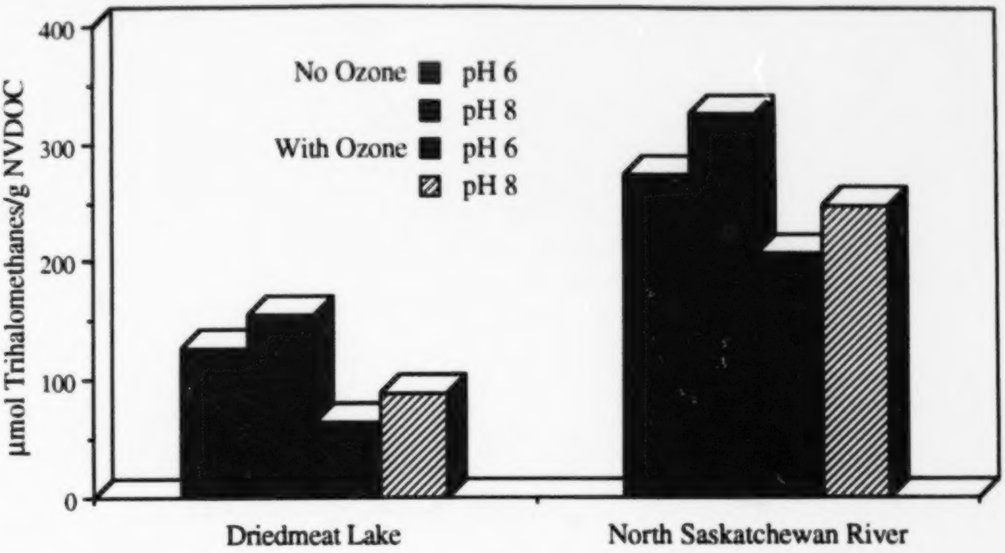


Figure VI.1 Effect of pH on Trihalomethanes Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

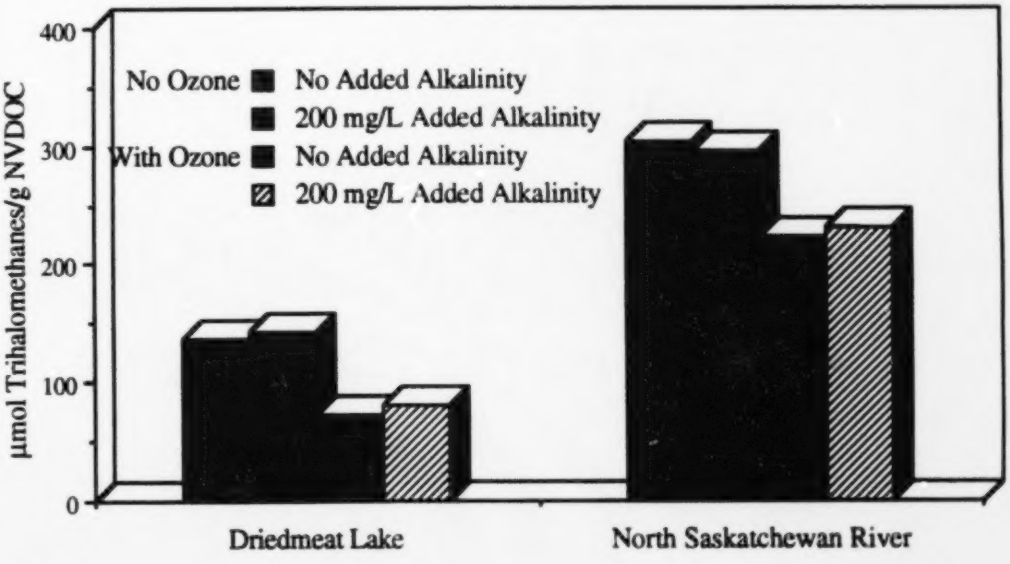


Figure VI.2 Effect of Alkalinity on Trihalomethanes Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

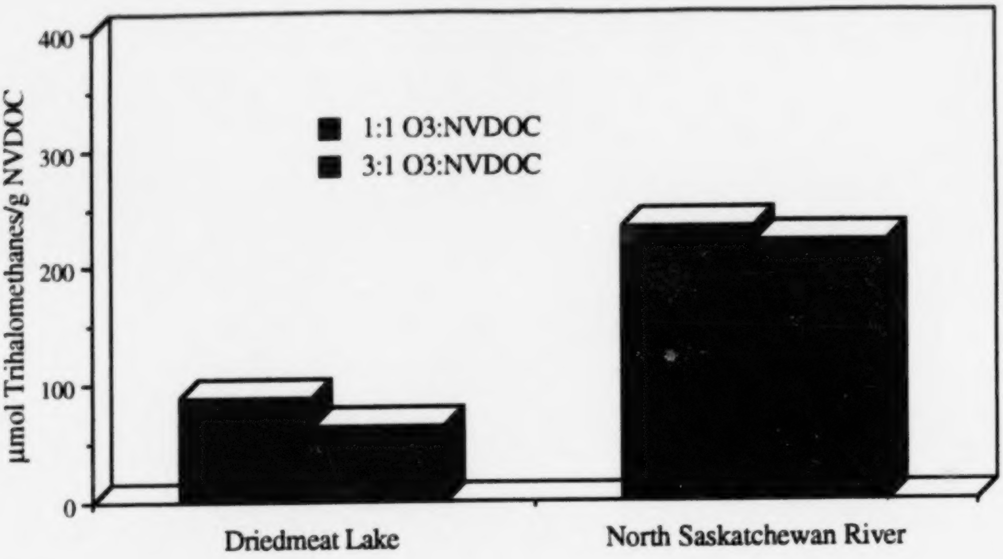


Figure VI.3 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Trihalomethanes Formation for Two Natural Waters which were Subsequently Chlorinated

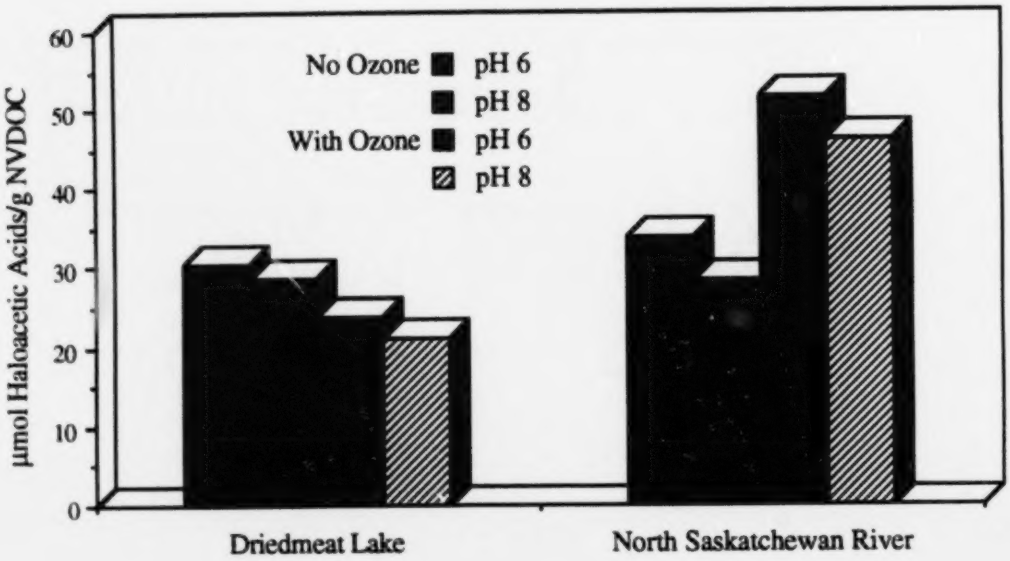


Figure VI.4 Effect of pH on Haloacetic Acids Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

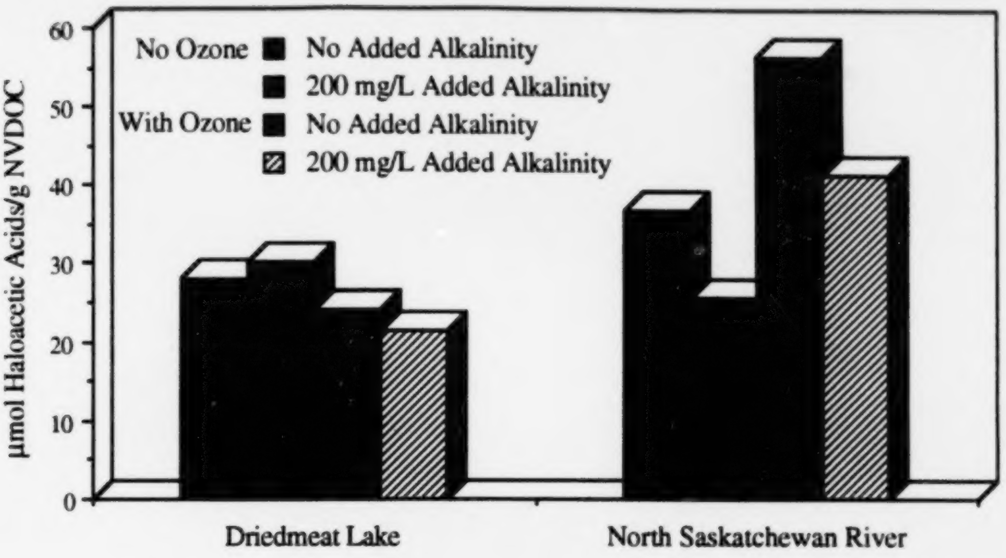


Figure VI.5 Effect of Alkalinity on Haloacetic Acids Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

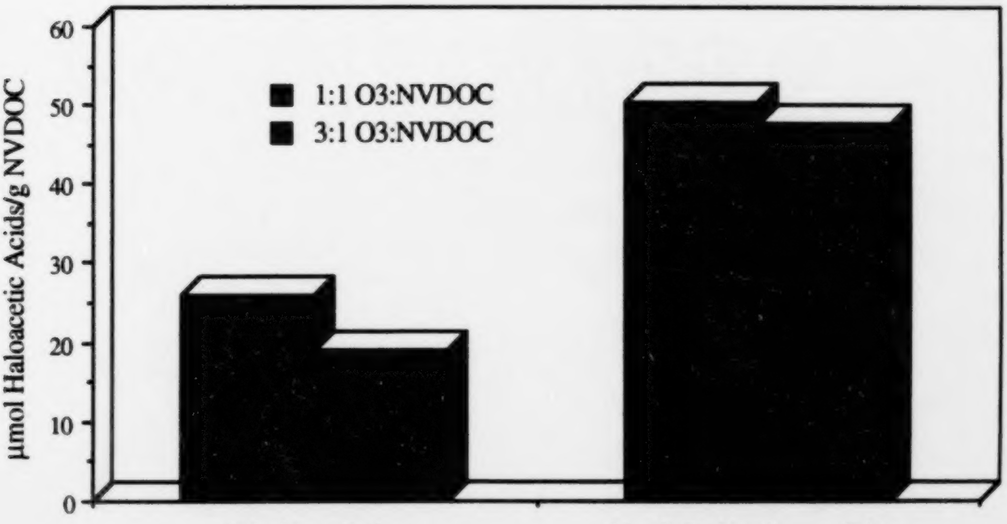


Figure VI.6 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Haloacetic Acids Formation for Two Natural Waters which were Subsequently Chlorinated

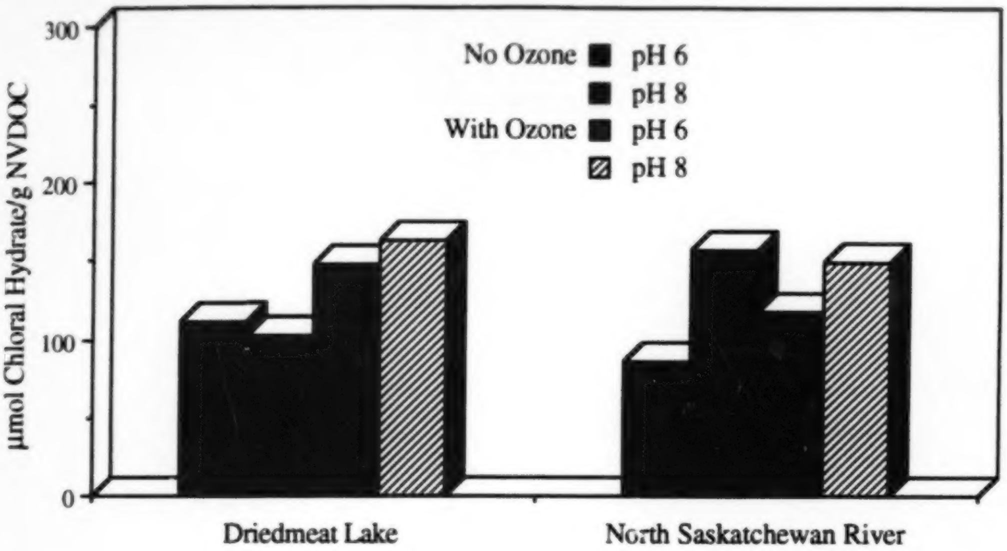


Figure VI.7 Effect of pH on Chloral Hydrate Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

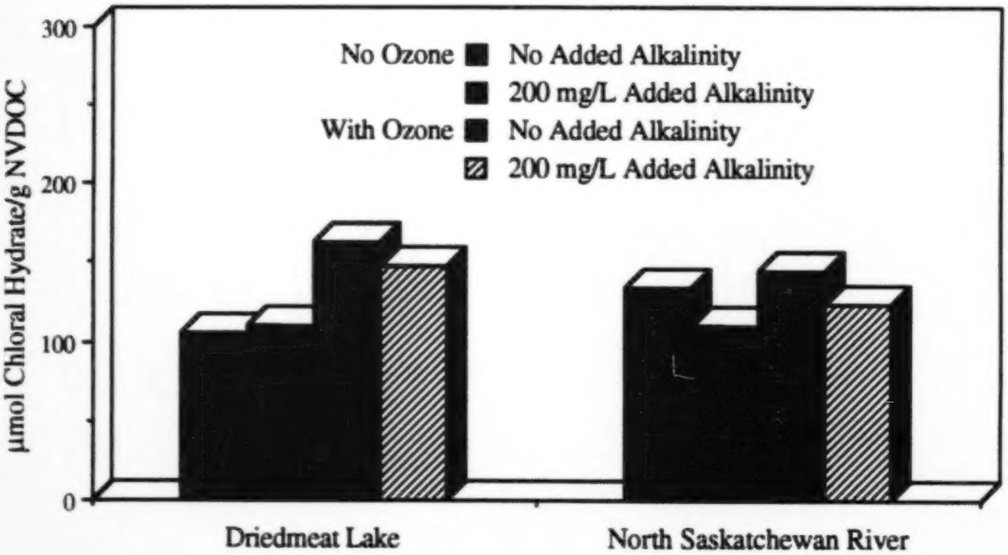


Figure VI.8 Effect of Alkalinity on Chloral Hydrate Formation or Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

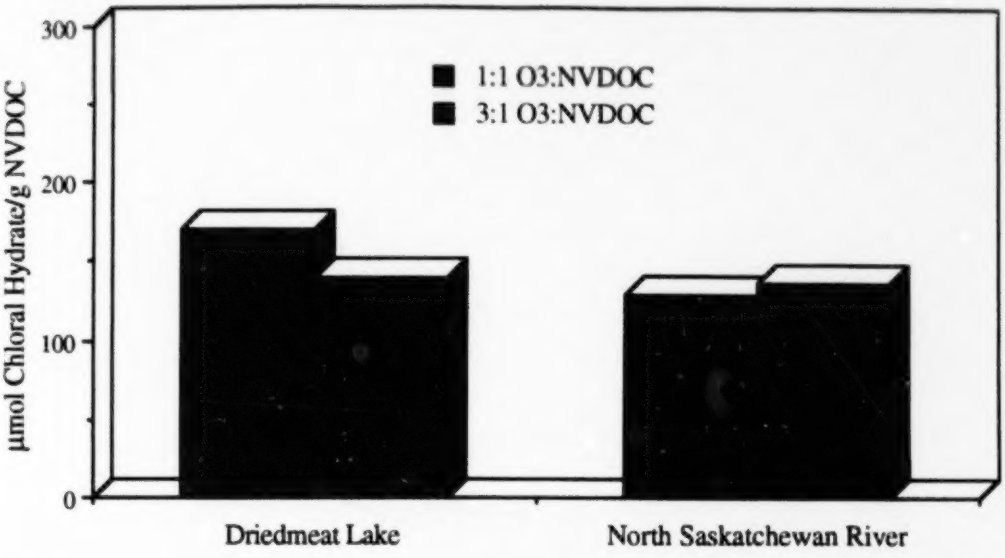


Figure VI.9 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Chloral Hydrate Formation for Two Natural Waters which were Subsequently Chlorinated

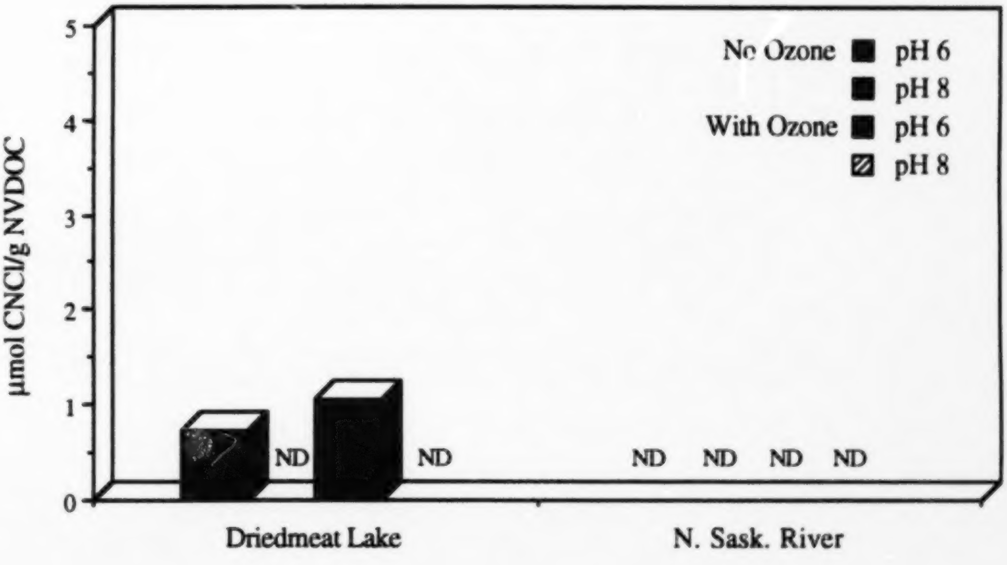


Figure VI.10 Effect of pH on Cyanogen Chloride Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

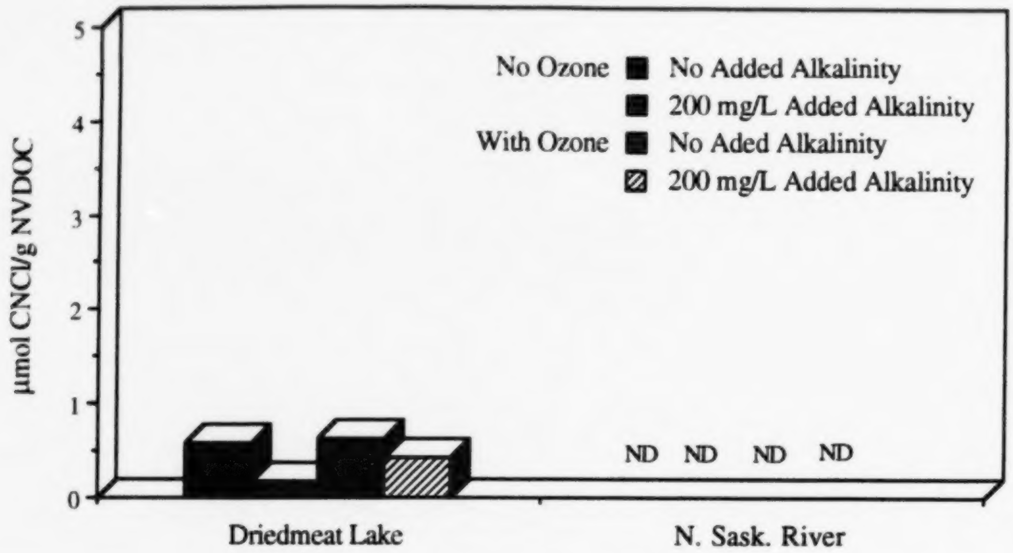


Figure VI.11 Effect of Alkalinity on Cyanogen Chloride Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chlorinated

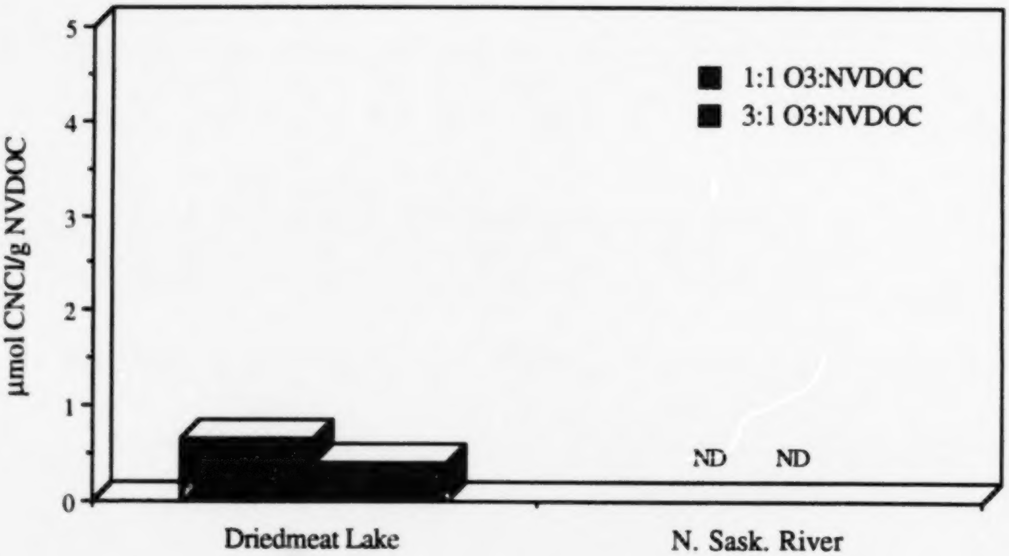


Figure VI.12 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Cyanogen Chloride Formation for Two Natural Waters which were Subsequently Chlorinated

Table VI.1 Confidence Intervals for Ozonation+Chlorination Factorials
Chlorine Demand Data

	DML8	DML4	NSR8	NSR4
Ozonation + Chlorination				
Midpoint s	0.89	1.12	0.63	0.51
95% CI	2.3	2.8	1.6	1.3
RCI	20%	14%	22%	6.5%
90% CI	1.3	1.6	0.94	0.74
RCI	12%	7.8%	12%	3.7%
Chlorination Without Ozonation				
Midpoint s	0.68	0.44	0.92	0.68
95% CI	1.7	1.1	2.3	1.7
RCI	9.7%	5.2%	12%	9.5%
90% CI	1.0	0.63	1.3	0.97
RCI	5.5%	2.9%	7.1%	5.4%
Net Change of Chlorine Demand on Ozonation				
Pooled midpoint s	0.39	0.42	0.58	0.30
95% CI	1.0	1.1	1.5	0.81
RCI	15%	99%	13%	39%
90% CI	0.56	0.62	0.83	0.43
RCI	8.5%	56%	7.3%	22%

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction

Table VI.2 Confidence Intervals for Ozonation+Chlorination Factorials
Cyanogen Chloride Data

NOM Fraction	s (μmol/g NVDOC)	95 % CI (μmol/g NVDOC)	RCI (%)	90 % CI (μmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	0.010	0.025	21	0.014	12
DML4	NA	NA	NA	NA	NA
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	0.010	0.026	6.9	0.015	3.9
NSR Raw	LDL	LDL	LDL	LDL	LDL
Experiments Employing Ozone					
DML8	LDL	LDL	LDL	LDL	LDL
DML4	LDL	LDL	LDL	LDL	LDL
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	0.114	0.289	54.9	0.164	31.1
NSR Raw	LDL	LDL	LDL	LDL	LDL

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

NA = Not analyzed

LDL = If present, concentrations were less than the detection limit

Table VI.3 Confidence Intervals for Ozonation+Chlorination Factorials
Chloral Hydrate Data

NOM Fraction	s (μmol/g NVDOC)	95 % CI (μmol/g NVDOC)	RCI (%)	90 % CI (μmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	4.76	12.1	6.17	6.90	3.48
DML4	12.2	31.0	11.0	17.6	6.24
NSR8	9.14	23.2	7.40	13.2	4.16
NSR4	4.71	12.0	4.67	6.83	2.71
DML Raw	3.77	9.56	8.87	5.36	5.01
NSR Raw	3.94	10.0	8.22	5.74	4.72
Experiments Employing Ozone					
DML8	15.3	38.8	10.5	22.0	5.89
DML4	8.41	21.4	5.01	12.1	2.94
NSR8	7.42	18.8	4.95	10.7	2.87
NSR4	12.0	30.6	6.12	17.3	3.49
DML Raw	13.5	34.2	22.0	19.4	12.4
NSR Raw	3.15	7.99	5.97	4.45	3.42

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

Table VI.4 Confidence Intervals for Ozonation+Chlorination Factorials
Haloacetic Acids Data

NOM Fraction	s (μmol/g NVDOC)	95 % CI (μmol/g NVDOC)	RCI (%)	90 % CI (μmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	29.0	73.8	24.7	41.8	14.0
DML4	1.22	3.13	1.93	1.78	1.08
NSR8	1.98	5.02	2.68	2.82	1.51
NSR4	4.28	10.9	7.19	6.23	4.11
DML Raw	1.05	2.67	4.51	1.46	2.57
NSR Raw	2.50	6.32	4.21	3.59	2.38
Experiments Employing Ozone					
DML8	15.2	38.6	14.7	21.9	8.26
DML4	6.33	16.1	6.50	9.13	3.74
NSR8	15.3	38.9	14.2	22.1	7.97
NSR4	7.71	19.6	22.2	11.1	12.6
DML Raw	0.52	1.28	2.89	0.80	1.73
NSR Raw	6.73	17.1	9.25	9.73	5.17

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

Table VI.5 Confidence Intervals for Ozonation+Chlorination Factorials
Trihalomethanes Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	66.2	168	20.4	95.3	11.6
DML4	67.9	173	22.6	97.8	12.8
NSR8	26.8	68.1	8.04	38.6	4.45
NSR4	20.4	51.8	6.89	29.3	3.89
DML Raw	8.06	20.5	7.27	11.6	4.16
NSR Raw	10.2	25.9	4.33	14.7	2.44
Experiments Employing Ozone					
DML8	26.5	67.2	18.9	38.1	10.7
DML4	22.7	57.7	8.21	32.7	4.74
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	5.99	15.2	10.0	8.59	5.57
NSR Raw	26.3	66.7	14.6	37.8	8.28

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

NA = Not analyzed

Table VI.6 DML Filtered Raw Water Ozonation+Chlorination Factorial - Raw Data

NVDOC = 16.35

10 min post-ozonation reaction time, 3:1 molar ratio chlorine to NVDOC, room temp., 7 d incubation

			DBP Peak Area Counts x 10^5									
pH	Alkalinity	mg O3 : mg C	CNCl	DBP I.S.	CH	BrAA	DCAA	TCAA	DBP IS	CHCl3	CHCl2Br	DBP IS
6	0	1	0.462	17.2	74.9	0.412	8.48	35.4	10.8	17.5	4.89	10.3
8	0	1	0.000	18.5	80.4	0.269	6.69	20.1	8.83	17.9	5.48	9.15
6	200	1	0.774	17.3	73.8	0.389	7.23	33.2	12.0	15.3	4.20	9.23
8	200	1	0.000	17.5	73.4	0.234	8.62	22.1	9.69	18.2	5.69	8.03
6	0	3	0.725	17.7	61.3	0.173	6.66	19.2	10.4	6.64	2.49	10.7
8	0	3	0.000	18.7	71.6	0.291	8.84	17.1	9.87	15.2	4.76	8.84
6	200	3	0.000	15.9	52.2	0.397	5.43	16.3	8.39	12.1	3.61	10.1
8	200	3	0.000	16.4	62.9	0.102	5.45	16.3	7.73	16.8	4.93	9.24
6.3	100	2	0.379	17.8	66.9	0.342	5.29	22.4	8.30	14.6	4.27	9.42
6.3	100	2	0.405	18.0	77.2	0.356	5.97	19.6	8.62	14.9	4.07	9.26
6.3	100	2	0.481	18.6	77.2	0.290	5.36	21.1	8.42	13.8	3.93	8.47
Standard			4.20	17.2	4.95	0.479	1.86	4.03	12.7	2.42	6.58	11.1
Blank			LDL	17.3	LDL	LDL	0.195	LDL	9.21	0.737	LDL	7.44
Spike			4.02	17.8	79.1	0.341	8.99	37.5	8.75	20.0	13.2	9.21
Sample Spiked			8-200-1	6 - 200 - 1		6 - 200 - 1				8 - 0 - 1		

		CNCl	DBP I.S.	CH	BrAA	DCAA	TCAA	DBP IS	CHCl3	CHCl2Br	DBP IS
Main Effects	pH	-0.490	NA	6.5	NA	0.45	-7.1	NA	4.1	1.42	NA
	Alkalinity	-0.103	NA	-6.5	NA	-0.99	-1.0	NA	1.3	0.20	NA
	mg O3: mg C	-0.128	NA	-13.6	NA	-1.16	-10.5	NA	-4.5	-1.12	NA
	Factorial Average	0.245	NA	68.8	NA	7.18	22	NA	15.0	4.51	NA
	Midpoint RSD (%)	12.6	NA	8.1	NA	6.8	6.7	NA	3.9	4.2	NA
Two Level Interactions	1,2	0.103	NA	-1.4	NA	0.26	1.6	NA	-0.3	-0.01	NA
	1,3	0.128	NA	4.0	NA	0.65	6.1	NA	2.5	0.38	NA
	2,3	-1.037	NA	-9.7	NA	-5.30	-3.5	NA	9.0	1.77	NA

* LDL or 0.00 = Less than Detection Limit   NA = Not Applicable

	CNCl	DBP I.S.	CH	BrAA	DCAA	TCAA	DBP	CHCl3	CHCl2Br	DBP
Nominal Standard Concentration (µg/L)	10.0	NA	24	NA	10.0	10.0	NA	20	20	NA
Standard Concentration (µg/L)	9.07	NA	25	NA	12.5	10.5	NA	20	18	NA
Blank	LDL	NA	LDL	NA	1.3	LDL	NA	LDL	LDL	NA
Spike Concentration (µg/L)	8.68	NA	40	NA	60	98	NA	234	35	NA

Table VI.7 DML Filtered Raw Water Ozonation+Chlorination Factorial - µg/mg NVDOC Data

16.35 mg/L NVDOC, 10 min post-ozonation reaction time, 3:1 molar ratio chlorine to NVDOC, room temp., 7 d incubation

			Concentration (µg DBP/mg NVDOC)					
pH	Alkalinity	mg O3:mg C	CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
6	0	1	0.061	23.0	3.50	5.65	12.5	0.802
8	0	1	0.000	24.6	2.76	3.21	12.8	0.898
6	200	1	0.102	22.6	2.98	5.31	10.8	0.688
8	200	1	0.000	22.5	3.56	3.53	13.0	0.933
6	0	3	0.096	18.8	2.75	3.06	4.36	0.408
8	0	3	0.000	21.9	3.65	2.73	10.8	0.780
6	200	3	0.000	16.0	2.24	2.60	8.45	0.592
8	200	3	0.000	19.3	2.25	2.60	12.0	0.808
6.3	100	2	0.050	20.5	2.18	3.58	10.3	0.700
6.3	100	2	0.054	23.7	2.46	3.13	10.5	0.667
6.3	100	2	0.064	23.7	2.21	3.37	9.71	0.644

Main Effects	pH	-0.065	2.0	0.19	-1.14	3.1	0.232
	Alkalinity	-0.014	-2.0	-0.41	-0.15	1.0	0.033
	mg O3: mg C	-0.017	-4.2	-0.48	-1.67	-3.4	-0.183
Factorial Average		0.032	21.1	2.96	3.59	10.6	0.739

Two Level Interactions	1,2	0.014	-0.4	0.11	0.25	-0.3	-0.002
	1,3	0.017	1.2	0.27	0.97	1.9	0.062
	2,3	-0.137	-3.0	-2.19	-0.57	6.7	0.290

* LDL or 0.00 = Less than Detection Limit

Table VI.8 DML Filtered Raw Water Ozonation+Chlorination Factorial - µmol/g NVDOC Data

16.35 mg/L NVDOC, 10 min post-ozonation reaction time, 3:1 molar ratio chlorine to NVDOC, room temp., 7 d incubation

			Concentration (µmol DBP/g NVDOC)					
pH	Alkalinity	mg O3:mg C	CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
6	0	1	0.993	170	27.2	34.6	169	10.8
8	0	1	0.00	182	21.4	19.6	173	12.1
6	200	1	1.66	167	23.2	32.5	146	9.30
8	200	1	0.00	166	27.6	21.6	176	12.6
6	0	3	1.56	139	21.3	18.8	58.9	5.52
8	0	3	0.00	162	28.3	16.7	145	10.5
6	200	3	0.00	118	17.4	15.9	114	8.00
8	200	3	0.00	142	17.5	15.9	162	10.9
6.3	100	2	0.815	151	16.9	21.9	139	9.46
6.3	100	2	0.871	175	19.1	19.2	142	9.02
6.3	100	2	1.03	175	17.2	20.6	131	8.71

		CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
Main Effects	pH	-1.05	15	1.4	-7.0	42	3.1
	Alkalinity	-0.22	-15	-3.2	-0.9	13	0.4
	mg O3: mg C	-0.27	-31	-3.7	-10.2	-46	-2.5
	Factorial Average	0.89	173	23.9	28.9	163	10.8

* LDL or 0.00 = Less than Detection Limit

		CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
Two Level Interactions	1,2	0.22	-3	0.8	1.5	-3	0.0
	1,3	0.27	9	2.1	5.9	25	0.8
	2,3	-2.23	-22	-17.0	-3.5	91	3.9

Mean Effects

Cyanogen Chloride	pH 6	1.05
	pH 8	0.00
	0 alk	0.64
	200 alk	0.42
	1 to 1	0.66
	3 to 1	0.39
Chloral Hydrate	pH 6	148
	pH 8	163
	0 alk	163
	200 alk	148
	1 to 1	171
	3 to 1	140

Haloacetic acids	pH 6	47.7
	pH 8	42.2
	0 alk	48.2
	200 alk	42.9
	1 to 1	51.9
	3 to 1	38.0
Trihalomethanes	pH 6	130
	pH 8	175
	0 alk	146
	200 alk	160
	1 to 1	177
	3 to 1	129

Total
Measured DBPFPs

pH 6	328
pH 8	381
0 alk	358
200 alk	351
1 to 1	401
3 to 1	307

APPENDIX VII

HALOGENATED DISINFECTION BY-PRODUCTS FROM OZONATION AND CHLORAMINATION OF ISOLATED NOM AND OF WATER FROM DRIEDMEAT LAKE AND THE NORTH SASKATCHEWAN RIVER

This appendix contains additional data pertaining to the factorial experiments examining the effects of pH, alkalinity and ozone dosage on subsequent halogenated disinfection by-product (XDBP) formation for the natural water samples described in Chapter 7.2. Samples were obtained from Driedmeat Lake and the North Saskatchewan River (NVDOC 16.35 and 1.67 mgC/L, respectively). Selected samples were first ozonated at a 1:1 or 3:1 applied ozone:NVDOC ratio, at pH 6 or 8, and either without additional alkalinity or with 200 mg/L as $CaCO_3$ added alkalinity (added as $NaHCO_3$). All were chloraminated at a 3:1 Cl_2:NVDOC ratio using reagent grade sodium hypochlorite and ammonium chloride (3:1 mass ratio) under the same pH and alkalinity conditions mentioned above. XDBPs measured included the trihalomethanes, haloacetic acids, chloral hydrate and cyanogen chloride.

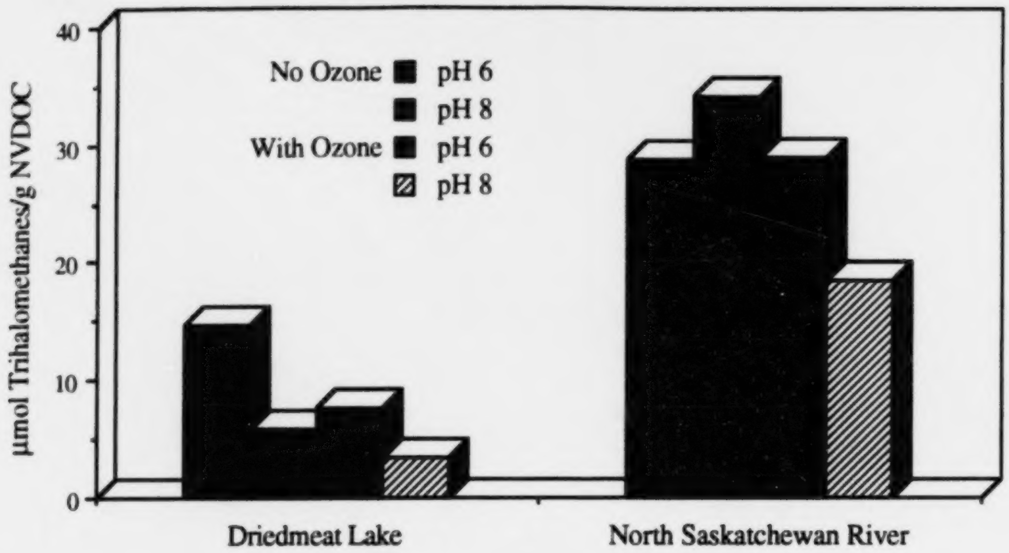


Figure VII.1 Effect of pH on Trihalomethanes Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

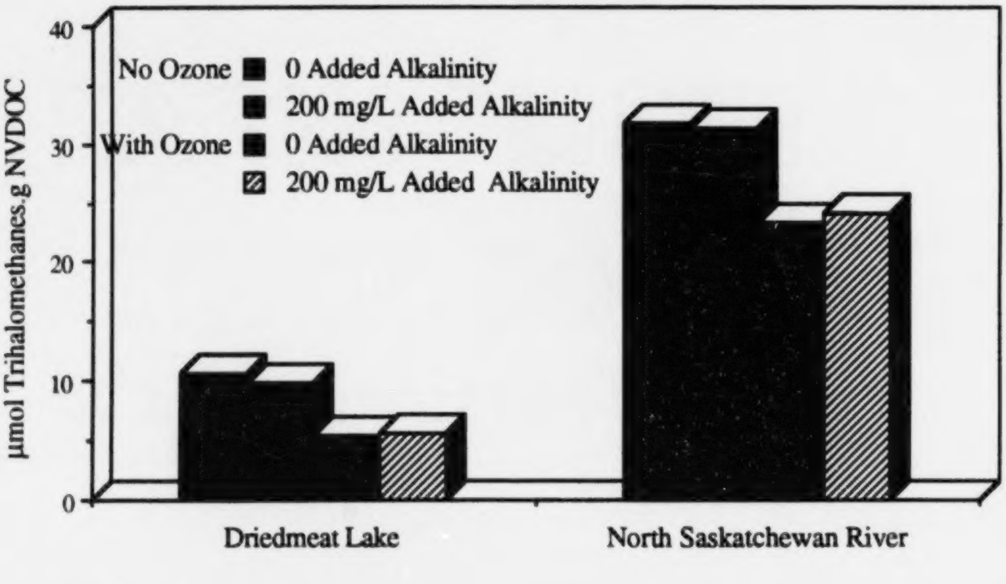


Figure VII.2 Effect of Alkalinity on Trihalomethanes Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

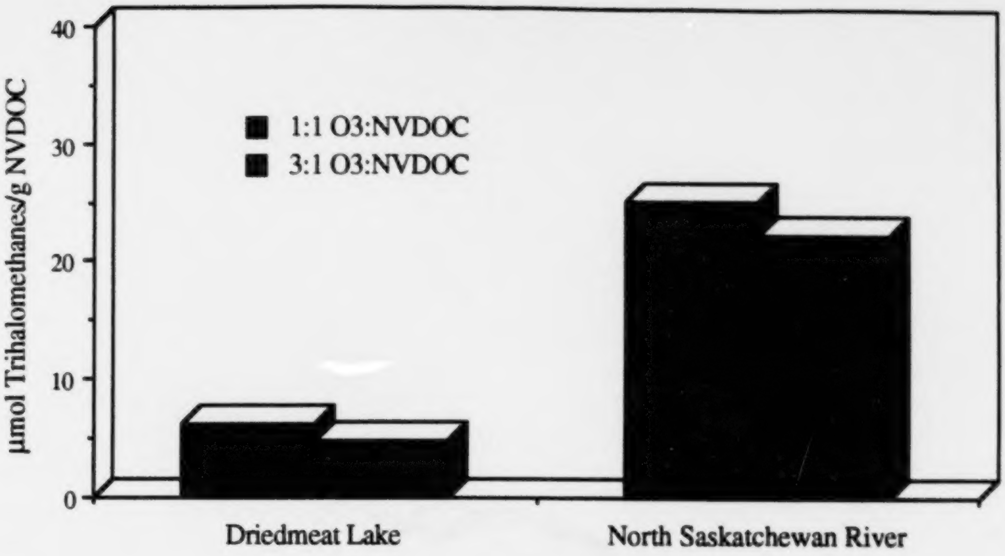


Figure VII.3 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Trihalomethanes Formation for Two Natural Waters which were Subsequently Chloraminated

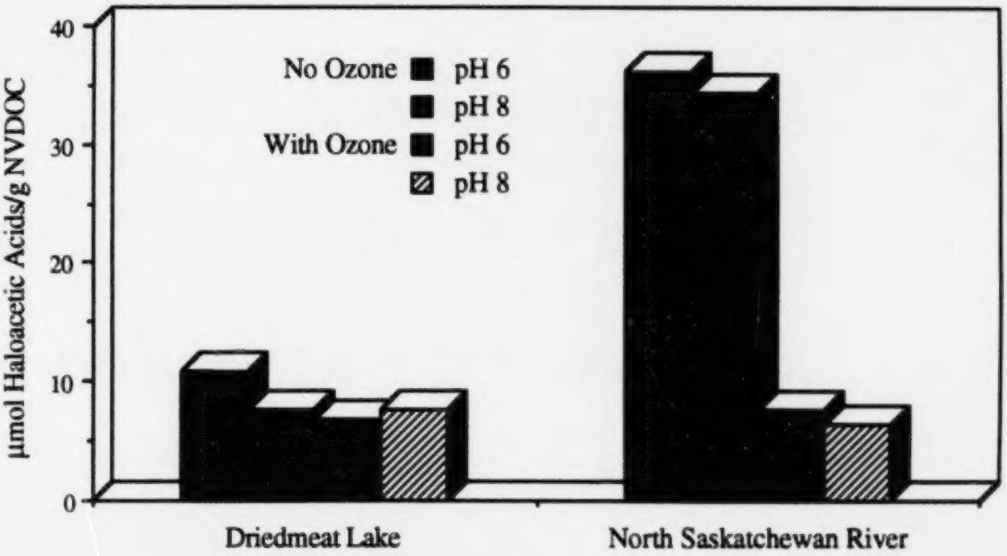


Figure VII.4 Effect of pH on Haloacetic Acids Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

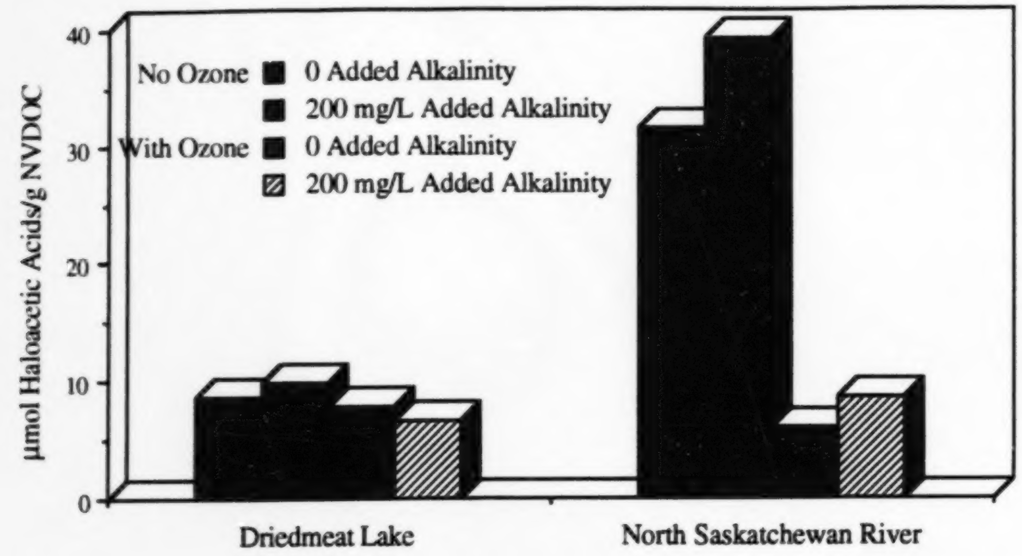


Figure VII.5 Effect of Alkalinity on Haloacetic Acids Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

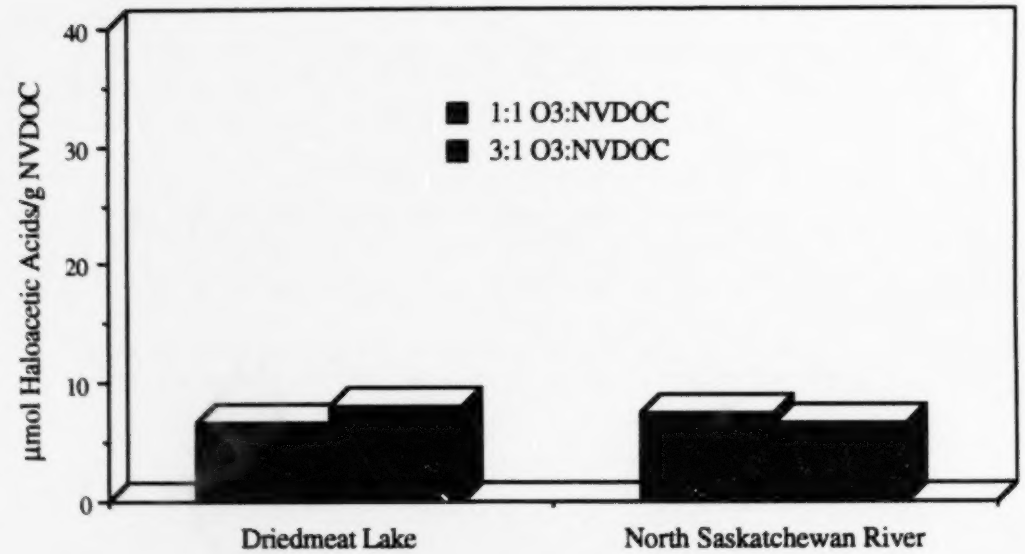


Figure VII.6 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Haloacetic Acids Formation for Two Natural Waters which were Subsequently Chloraminated

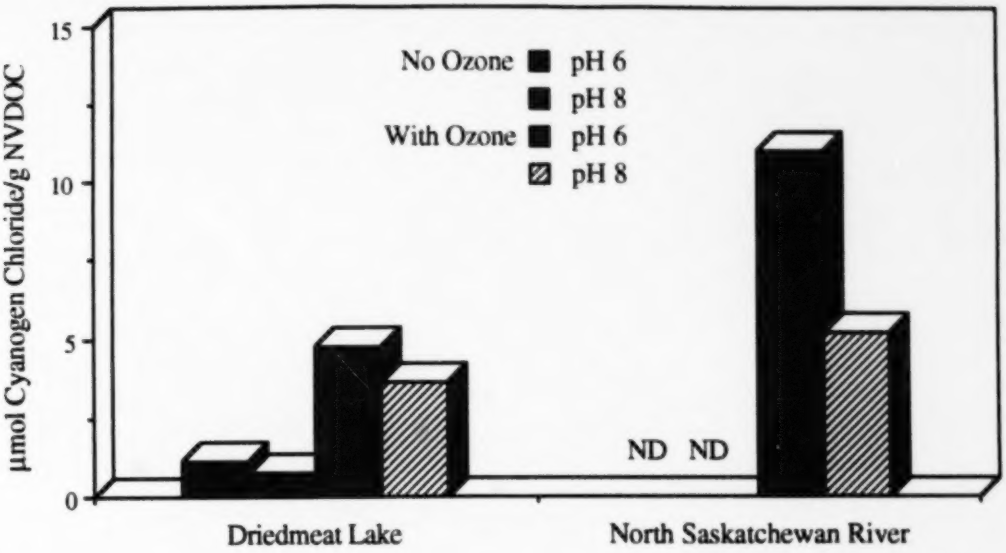


Figure VII.7 Effect of pH on Cyanogen Chloride Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

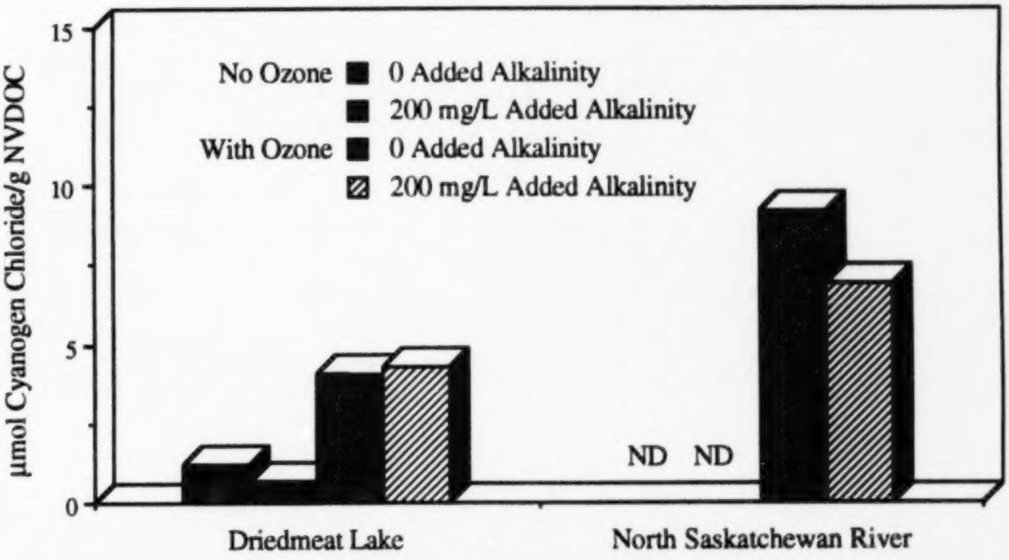


Figure VII.8 Effect of Alkalinity on Cyanogen Chloride Formation for Ozonated (2:1 O_3:NVDOC) and Natural Waters which were Subsequently Chloraminated

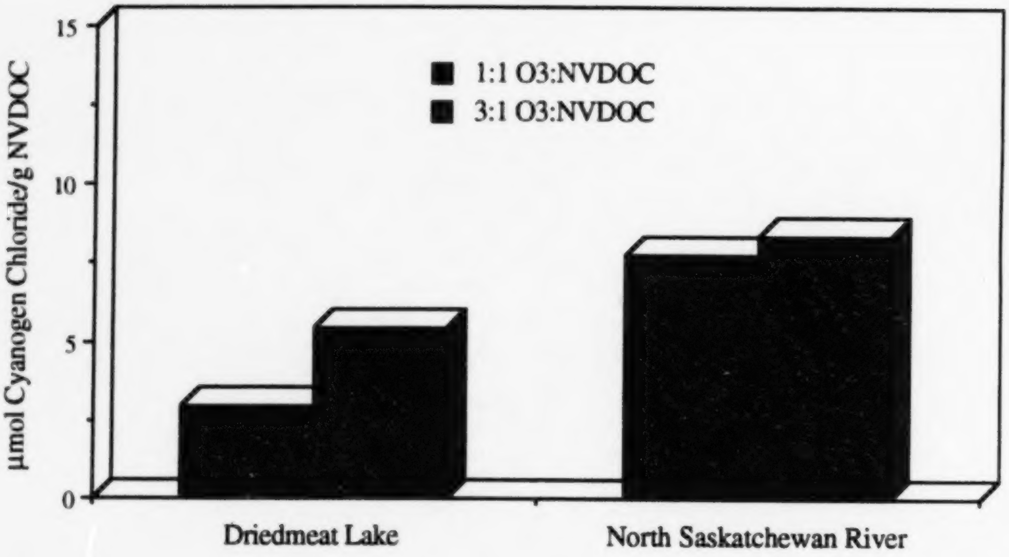


Figure VII.9 Effect of Ozone Doses Between 1:1 and 3:1 O_3:NVDOC on Cyanogen Chloride Formation for Two Natural Waters which were Subsequently Chloraminated

Table VII.1 Confidence Intervals for Ozonation+Chloramination Factorials
Cyanogen Chloride Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	0.518	1.32	15.3	0.746	8.72
DML4	0.348	0.884	11.4	0.501	6.55
NSR8	0.298	0.758	7.89	0.430	4.45
NSR4	0.070	0.179	1.66	0.101	1.02
DML Raw	0.030	0.077	8.0	0.044	4.5
NSR Raw	LDL	LDL	LDL	LDL	LDL
Experiments Employing Ozone					
DML8	0.672	1.71	13.4	0.967	7.61
DML4	0.383	0.972	4.50	0.551	2.58
NSR8	0.351	0.892	15.9	0.506	8.97
NSR4	0.419	1.06	16.4	0.603	9.32
DML Raw	0.273	0.693	16.5	0.393	9.44
NSR Raw	0.300	0.762	9.41	0.432	5.37

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

LDL = If present, concentrations were less than the detection limit

Table VII.2 Confidence Intervals for Ozonation+Chloramination Factorials
Chloral Hydrate Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	0.45	1.1	7.4	0.64	4.2
DML4	0.62	1.6	11	0.90	6.3
NSR8	0.97	2.5	23	1.4	13
NSR4	0.10	0.27	2.4	0.15	1.4
DML Raw	0.17	0.44	18	0.25	10
NSR Raw	2.23	5.67	5.33	3.23	3.02
Experiments Employing Ozone					
DML8	1.31	3.31	21.0	1.88	11.9
DML4	0.46	1.2	13	0.67	7.1
NSR8	0.45	1.1	11	0.71	6.3
NSR4	0.73	1.9	17	1.0	9.7
DML Raw	0.38	1.0	15	0.55	8.3
NSR Raw	0.21	0.53	40	0.30	23

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

Table VII.3 Confidence Intervals for Ozonation+Chloramination Factorials
Haloacetic Acids Data

NOM Fraction	s (μmol/g NVDOC)	95 % CI (μmol/g NVDOC)	RCI (%)	90 % CI (μmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	3.33	8.47	7.86	4.82	4.54
DML4	NA	NA	NA	NA	NA
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	0.50	1.3	6.8	0.72	3.9
NSR Raw	13.5	34.2	18.4	19.4	10.4
Experiments Employing Ozone					
DML8	1.46	3.66	6.39	2.12	3.64
DML4	3.47	8.81	22.7	4.96	12.8
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	0.85	2.2	15	1.2	8.4
NSR Raw	0.57	1.5	9.4	0.82	5.4

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

NA = Not analyzed

Table VII.4 Confidence Intervals for Ozonation+Chloramination Factorials
Trihalomethanes Data

NOM Fraction	s (µmol/g NVDOC)	95 % CI (µmol/g NVDOC)	RCI (%)	90 % CI (µmol/g NVDOC)	RCI (%)
Experiments Without Ozone					
DML8	8.84	22.5	19.7	12.7	11.2
DML4	2.90	7.44	11.3	4.12	6.43
NSR8	2.10	5.29	6.82	2.97	3.89
NSR4	1.16	2.92	4.23	1.72	2.38
DML Raw	1.35	3.36	16.7	1.92	9.42
NSR Raw	13.3	33.7	5.34	19.1	3.04
Experiments Employing Ozone					
DML8	1.00	2.51	4.85	1.42	2.75
DML4	NA	NA	NA	NA	NA
NSR8	NA	NA	NA	NA	NA
NSR4	NA	NA	NA	NA	NA
DML Raw	0.81	2.1	19	1.2	11
NSR Raw	1.40	3.63	7.52	2.02	4.27

CI = confidence interval, 6 degrees of freedom, 90 or 95 % level of confidence
RCI = confidence interval expressed as % relative to mean effects

DML = Driedmeat Lake; NSR = North Saskatchewan River
8 or 4 = XAD-8 or XAD-4 resin fraction
DML Raw and NSR Raw refer to filtered raw waters

NA = Not analyzed

Table VII.5 DML Filtered Raw Water Ozonation+Chloramination Factorial - Raw Data

NVDOC = 16.35

10 min post-ozonation reaction time, 3:1 molar ratio chlorine to NVDOC, room temp., 7 d incubation

			DBP Peak Area Counts x 10^5									
pH	Alkalinity	mg O3 : mg C	CNCl	DBP IS	CH	BrAA	DCAA	TCAA	DBP IS	CHCl3	CHCl2Br	DBP IS
6	0	1	1.14	19.1	4.49	0.169	3.78	1.69	8.44	2.37	0.486	9.63
8	0	1	1.31	19.6	2.48	0.183	2.72	2.07	9.77	1.74	0.0979	9.44
6	200	1	1.96	18.1	4.31	0.138	3.76	2.05	9.19	2.49	0.551	9.47
8	200	1	1.03	16.9	1.83	0.194	3.45	2.77	9.30	1.34	0.0446	8.08
6	0	3	2.82	17.5	3.03	0.108	5.11	2.00	9.57	2.05	0.304	8.85
8	0	3	2.27	19.7	2.42	0.173	5.17	2.84	10.3	1.17	0.0231	8.99
6	200	3	2.89	18.5	3.00	0.129	2.27	1.48	8.81	2.10	0.169	8.89
8	200	3	2.18	17.6	1.89	0.121	4.63	2.35	9.62	1.65	0.0671	9.08
6.3	100	2	1.60	17.7	3.47	0.191	4.50	2.31	10.7	1.89	0.248	8.28
6.3	100	2	1.83	16.7	3.22	0.209	3.89	2.73	9.86	1.96	0.294	8.91
6.3	100	2	1.80	15.9	3.54	0.247	4.31	2.76	10.9	1.80	0.294	9.84
Standard			4.20	17.2	4.95	0.479	1.86	4.03	12.7	2.42	6.58	11.1
Blank			LDL	17.3	LDL	LDL	0.195	LDL	9.21	0.74	LDL	7.44

Main Effects	pH	-0.51	NA	-1.55	NA	0.26	0.70	NA	-0.78	-0.319	NA
	Alkalinity	0.13	NA	-0.35	NA	-0.67	0.01	NA	0.06	-0.020	NA
	mg O3: mg C	1.18	NA	-0.69	NA	0.87	0.02	NA	-0.24	-0.154	NA
	Factorial Average	1.95	NA	2.93	NA	3.86	2.16	NA	1.86	0.218	NA
	Midpoint RSD (%)	7.3	NA	4.9	NA	7.4	9.7	NA	4.3	9.5	NA

Two Level Interactions	1,2	-0.32	NA	-0.24	NA	0.76	0.09	NA	-0.02	0.015	NA
	1,3	-0.13	NA	0.69	NA	0.95	0.15	NA	0.11	0.128	NA
	2,3	-0.56	NA	0.27	NA	-4.09	-2.07	NA	0.81	-0.103	NA

* LDL = Less than Detection Limit NA = Not Applicable

	CNCl	DBP	CH	BrAA	DCAA	TCAA	DBP	CHCl3	CHCl2Br	DBP
Nominal Standard Concentration (µg/L)	10.0	NA	24	NA	10.0	10.0	NA	20	20	NA
Standard Concentration (µg/L)	9.07	NA	25	NA	12.5	10.5	NA	20	18	NA
Blank	LDL	NA	LDL	NA	1.3	LDL	NA	LDL	LDL	NA

Table VII.6 DML Filtered Raw Water Ozonation+Chloramination Factorial - μg/mg NVDOC Data

16.35 mg/L NVDOC, 10 min post-ozonation reaction time, 3:1 molar ratio chloramine to NVDOC, room temp., 7 d incubation

			Concentration (μg DBP/mg NVDOC)					
pH	Alkalinity	mg O3:mg C	CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
6	0	1	0.151	1.38	1.56	0.270	1.16	0.0797
8	0	1	0.173	0.760	1.12	0.330	0.690	0.0160
6	200	1	0.259	1.32	1.55	0.327	1.25	0.0903
8	200	1	0.136	0.561	1.42	0.442	0.391	0.0073
6	0	3	0.373	0.928	2.11	0.319	0.922	0.0498
8	0	3	0.300	0.742	2.13	0.453	0.264	0.0038
6	200	3	0.382	0.919	0.937	0.236	0.959	0.0277
8	200	3	0.288	0.579	1.91	0.375	0.623	0.0110
6.3	100	2	0.211	1.06	1.86	0.369	0.802	0.0407
6.3	100	2	0.242	0.987	1.61	0.436	0.854	0.0482
6.3	100	2	0.238	1.08	1.78	0.441	0.735	0.0482

Main Effects	pH	-0.067	-0.476	0.11	0.112	-0.582	-0.0523
	Alkalinity	0.017	-0.106	-0.28	0.002	0.047	-0.0032
	mg O3: mg C	0.156	-0.212	0.36	0.004	-0.181	-0.0253
	Factorial Average	0.258	0.898	1.59	0.344	0.782	0.0357

Two Level Interactions	1,2	-0.042	-0.074	0.31	0.015	-0.017	0.0025
	1,3	-0.017	0.212	0.39	0.024	0.084	0.0210
	2,3	-0.074	0.083	-1.69	-0.330	0.606	-0.0168

Table VII.7 DML Filtered Raw Water Ozonation+Chloramination Factorial - µmol/g NVDOC Data

16.35 mg/L NVDOC, 10 min post-ozonation reaction time, 3:1 molar ratio chloramine to NVDOC, room temp., 7 d incubation

			Concentration (µmol DBP/g NVDOC)					
pH	Alkalinity	mg O3:mg C	CNCl	CH	DCAA	TCAA	CHCl3	CHCl2Br
6	0	1	2.45	10.2	12.1	1.65	15.7	1.08
8	0	1	2.82	5.61	8.71	2.02	9.32	0.217
6	200	1	4.21	9.76	12.0	2.00	16.9	1.22
8	200	1	2.21	4.14	11.0	2.71	5.28	0.099
6	0	3	6.06	6.86	16.4	1.95	12.5	0.673
8	0	3	4.88	5.48	16.6	2.78	3.56	0.051
6	200	3	6.21	6.79	7.27	1.45	13.0	0.374
8	200	3	4.69	4.28	14.8	2.30	8.41	0.149
6.3	100	2	3.44	7.86	14.4	2.26	10.8	0.549
6.3	100	2	3.94	7.29	12.5	2.67	11.5	0.651
6.3	100	2	3.88	8.01	13.8	2.70	9.93	0.651
Main Effects		pH	-1.09	-3.51	0.8	0.69	-7.86	-0.707
		Alkalinity	0.28	-0.79	-2.1	0.01	0.63	-0.044
		mg O3: mg C	2.54	-1.57	2.8	0.02	-2.45	-0.341
		Factorial Average	3.16	8.51	11.0	1.89	13.97	0.838
Two Level Interactions		1,2	-0.68	-0.55	2.4	0.09	-0.23	0.034
		1,3	-0.27	1.57	3.0	0.15	1.14	0.283
		2,3	-1.20	0.61	-13.1	-2.02	8.19	-0.227

Mean Effects

Cyanogen Chloride	pH 6	4.74
	pH 8	3.65
	0 alk	4.05
	200 alk	4.33
	1 to 1	2.92
	3 to 1	5.46
Chloral Hydrate	pH 6	8.39
	pH 8	4.88
	0 alk	7.03
	200 alk	6.24
	1 to 1	7.42
	3 to 1	5.85

Haloacetic acids	pH 6	13.7
	pH 8	15.2
	0 alk	15.5
	200 alk	13.4
	1 to 1	13.1
	3 to 1	15.9
Trihalomethanes	pH 6	15.3
	pH 8	6.77
	0 alk	10.8
	200 alk	11.4
	1 to 1	12.5
	3 to 1	9.66

Total
Measured DBPFPs

pH 6	42.2
pH 8	30.5
0 alk	37.4
200 alk	35.3
1 to 1	35.9
3 to 1	36.8